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Activated Carbon Treatment of Industrial Wastewaters Selected Technical Papers

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Aug 79

United States
Environmental Protection
Agency

Robert S. Kerr Environmental Research
Laboratory
Ada OK 74820

EPA-600/2-79-177
August 1979

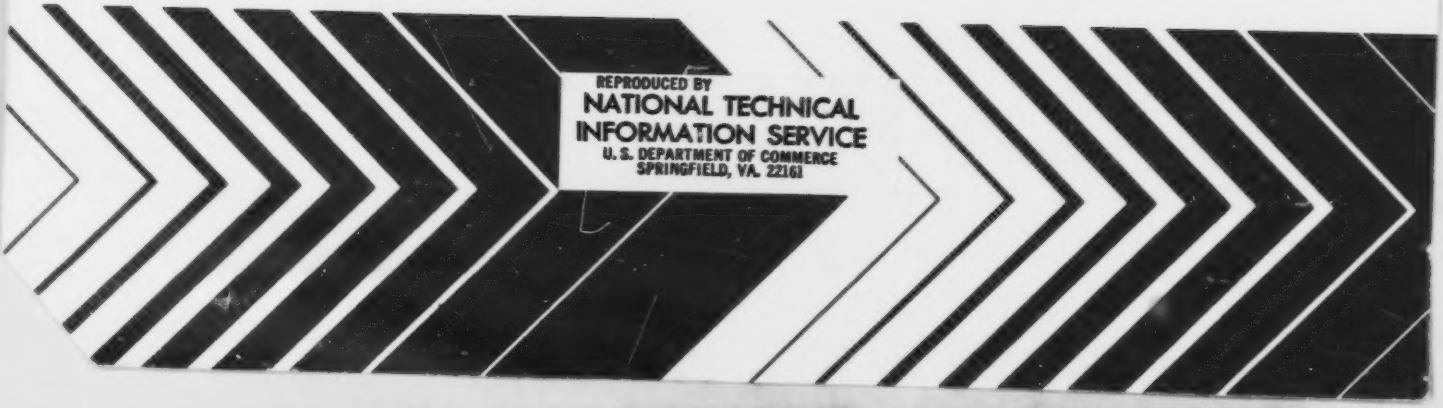
Research and Development

PB80-100522

EPA

Activated Carbon Treatment of Industrial Wastewaters

Selected Technical Papers



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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/2-79-177

2.

3. RECIPIENT'S ACCESSION NO.
PB80-100522

4. TITLE AND SUBTITLE
Activated Carbon Treatment of Industrial Wastewaters - Selected Technical Papers

5. REPORT DATE
August 1979 issuing date

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Edited by:
Industrial Sources Section, Source Management Branch
Robert S. Kerr Environmental Research Laboratory

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Industrial Sources Section - Source Management Branch
Robert S. Kerr Environmental Research Laboratory
P.O. Box 1198
Ada, Oklahoma 74820

10. PROGRAM ELEMENT NO.
1BB610

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Robert S. Kerr Environmental Research Laboratory
U.S. Environmental Protection Agency
P.O. Box 1198
Ada, OK 74820

13. TYPE OF REPORT AND PERIOD COVERED
In-House

14. SPONSORING AGENCY CODE
EPA 600/15

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Because of the tremendous interest in the organic constituent removal by activated carbon, the two industrial categories displaying the most interest are the petroleum refining and petrochemical industries. EPA's Office of Research and Development has co-sponsored two technical symposia for the petroleum refining/petrochemical industries, and activated carbon treatment as an important section of both agendas. The technical papers presented research activities conducted by consultants, industries, and EPA.

The presentations made at these symposia have been arranged into the following sequence: (1) State-of-the-Art, (2) Organic Compound Removal, (3) Granular Pilot-Scale Studies, (4) Powdered Activated Carbon Pilot-Scale Studies, (5) Full-Scale Granular Activated Carbon Treatment, (6) Full-Scale Powdered Activated Carbon Treatment, and (7) Activated Carbon Regeneration.

Economics of Activated Carbon Treatment are presented in the applicable individual technical papers and is not a separate topic for this report.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Activated Carbon	Industrial Waste Treatment	Processes & Effects	68-D
Mixed Media Filter		Characterization	71-C
Environmental Engineering		Measurement & Monitoring	89-B
Chemical Engineering		Bench-Scale Plants	94-E
Organic Chemistry			97-R
Refining	Petrochemical Industry		
Refining Wastewaters			

18. DISTRIBUTION STATEMENT
Release to public

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
307

22. PRICE
PC A14 / MF A01

EPA Form 2220-1 (9-73)

*U.S. GOVERNMENT PRINTING OFFICE: 1979 0-620-007/6322

EPA-600/2-79-177
August 1979

ACTIVATED CARBON TREATMENT OF INDUSTRIAL WASTEWATERS
SELECTED TECHNICAL PAPERS

Edited By

Industrial Sources Section
Source Management Branch
Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma 74820

OFFICE OF ENERGY, MINERALS, AND INDUSTRY
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American public.

W. C. Galegar

W. C. Galegar
Director
Robert S. Kerr Environmental Research Laboratory

ABSTRACT

Historically, activated carbon has been used to remove taste and odor constituents in drinking water, or to decolorize granular sugar. Industrial wastewater treatment employing granular activated carbon was basically a technical curiosity until the 1970's. During this decade, the articles as well as claims for and against activated carbon treatment for industrial wastewaters are increasing at a phenomenal rate.

EPA's Office of Research and Development, has been vitally interested in this treatment technology, from the technical standpoint as well as furnishing a technical data base to the Federal and State guidelines and permit program. Other prime users of the technical data base are industry, consultants and academia.

Because of the tremendous interest in the organic constituent removal by activated carbon, the two industrial categories displaying the most interest are the petroleum refining and petrochemical industries. EPA's Office of Research and Development has co-sponsored two technical symposia for the petroleum refining/petrochemical industries, and activated carbon treatment as an important section of both agendas. The technical papers presented research activities conducted by consultants, industries, and EPA.

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SECTION 1
ACTIVATED CARBON STATE OF THE ART

"CURRENT STATE OF THE ART OF ACTIVATED CARBON TREATMENT"

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The treatment of wastewaters using activated carbon has received wide attention for several years - more recently catalyzed by the development of effluent quality guidelines pursuant to Public Law 92-500. These effluent quality criteria and the accompanying development documents prominently mention carbon as an applicable and attractive treatment concept, particularly in the Best Available Treatment Economically Achievable (BATEA) process mode currently stated as necessary to produce the 1983 quality level objective. Until recently, most of the literature has dealt with exploring theoretical concepts and documenting experimental results. As more information on full-scale operations is becoming available, however, it is considered appropriate to review the current state of the art of activated carbon treatment - both in municipal and industrial sectors. It is the purpose of this treatise, therefore, to present pertinent and current information relative to the activated carbon treatment of municipal and industrial wastewaters. A brief discussion of adsorption concepts and carbon characteristics also is included.

ADSORPTION CONCEPTS AND THEORY

Molecules are held together by cohesive forces ranging from strong valence bonds to the weaker van Der Waals forces of attraction. These attractive forces are satisfied in the solid phase interior molecules, having the ability to capture certain fluid molecules as they contact the surface. van Der Waals forces are the bases for the adsorption of wastewater constituents onto carbon which has been activated to maximize this interphase accumulation of liquid constituents at the surface or interphase of the solid phase.

The rate at which substances are removed from the liquid phase (adsorbate) to the solid phase (adsorbent) is of paramount importance when evaluating the efficacy of activated carbon as a wastewater treatment process. Unfortunately, the task of quantifying the many forces acting at the solid-liquid interface is a formidable one. Developing a mathematical expression which describes the dynamic phenomenon occurring in a continuous-flow/fixed-bed reactor has been difficult because of multi-variable influences. The overall adsorption rate represents the combined effects of diffusion through a laminar layer of fluid surrounding the constituent, surface diffusion, and adsorption on the internal pore surfaces. Most mathematical solutions for equations which describe concentration/time profiles are limited to the special case in which only one of these phenomena controls the overall rate of adsorption (1).

One expression for the continuous-flow regime assumes the diffusion of the constituent through the liquid phase and through the pores of the carbon (which are rate-limiting), then combining these resistances in an overall mass coefficient term. Using this rationale:

$$q\frac{dC}{dD} = k_2 r(C_s - C) \qquad \text{(Eq. 1)}$$

where:

q = flow rate
C_s = concentration of the adsorbate
D = adsorbent bed depth
C = equilibrium adsorbate concentration
k_2r = overall mass transfer coefficient

A more convenient expression of Equation 1 is in terms of the adsorbate rate with respect to the weight of the carbon in the columns:

$$q\,dC/dM = k_2r/X\ (C_s-C) \qquad \text{(Eq. 2)}$$

where:

M = weight of the carbon in the column
X = packed density of the carbon in the column

Another proposed model predicts four successively decreasing adsorption rates would be observed as the adsorption proceeds to equilibrium. The initial rate would be limited by the rate of adsorbate transfer across the film layer, film diffusion, or, if sufficient turbulence existed, control would be exerted by the combined rate of external surface adsorption and macropore filling. After the external surface adsorption capacity was exhausted, there would exist three secondary adsorption rates controlled, respectively, by the filling of the macropore (an effective radius of 5,000 to 20,000 A^o), the transitional pore (20 to 100 A^o), and the micropore (10 to 20 A^o effective radius). This model is illustrated in Figure 1 (2). It is inherent in this model that the intraparticle transport occurs as a series of adsorption/desorption steps, each linear with respect to time, and their summation resulting in a time/linear function.

The development of adsorbate removal kinetics on a batch basis can be used to approximate carbon effectiveness and predict organic residual levels. The adsorption isotherm is used for this purpose and is defined as a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at a constant temperature. The isotherm is expressed in terms of removal of an impurity - such as BOD, COD, and color - per unit weight of carbon as a function of the equilibrium impurity remaining in solution. Linear plots as shown in Figure 2 can be expressed in terms of the empirical Freundlich equation. This expression relates the amount of impurity in the adsorbed phase to that in solution:

$$\frac{X}{M} = KC^{1/n} \qquad \text{(Eq. 3)}$$

where:

X = amount of impurity adsorbed
M = weight of carbon
C = equilibrium concentration of impurity in solution
K,n = constants

The Freundlich isotherm is valid within the context of a batch test for pure substances and some dilute wastewaters. As shown in Figure 2, its application is limited in certain cases when a significant portion of the organic impurities are not amenable to sorption, resulting in a constant residual, regardless of the carbon dosage.

The constants "n" and "K" can be used to define both the nature of the carbon and the adsorbate. A high "K" and "n" value, for example, indicate good adsorption throughout the concentration range studied. A low "K" and "n" value would infer low adsorption at dilute concentrations with high adsorption at the more concentrated levels. Variations of the constants for selected wastewaters are shown in Table 1 (3).

FACTORS WHICH INFLUENCE ADSORPTION

There are many factors which influence both the rate and magnitude of adsorption - underscoring the difficulty in developing predictive models which would apply to all complex wastewaters. A brief discussion of the more important factors is presented herein.

Molecular Structure. The molecular structure, or nature of the adsorbate, is particularly important in dictating the degree of adsorption that can actually occur. As a rule, branched-chain compounds are more sorbable than straight-chain compounds, the type and location of the substituent (functional) group affects adsorbability, and molecules which are low in polarity and solubility tend to be preferentially adsorbed. Unless the screening action of the carbon pores actually impedes, large molecules are more sorbable than small molecules of similar chemical nature. This is attributable to more solute chemical bonds being formed, making desorption more difficult.

Inorganic compounds demonstrate a wide range of adsorbability. Disassociated salts - such as potassium chloride and sodium sulfate - are essentially nonsorbable. Mercuric chloride and ferric chloride are relatively sorbable, and iodine is one of the most adsorbable substances known. Generally, however, a significant reduction in inorganic materials is not expected in carbon systems.

Organic compound sorbability can be classified to some extent. Primary alcohols and sugars, for example, are resistant to adsorption, while ethers and certain organic acids are highly sorbable. Recently published experimental data presented in Table 2 are indicative of the sorbability of many organic compounds (4). Additional sorbability data conducted independently are presented in Table 3.

Solubility. An increase in solubility acts to oppose the attraction of the adsorbate to carbon. Thus, polar groups which have a high affinity for water usually diminish adsorption from aqueous solutions. Conversely, the greater adsorption of the higher aliphatic acids and alcohols is attributed in part of their relatively lower solubility in an aqueous solution. There are exceptions to this, as in the case of the highly soluble chloracetic acid (5).

Ionization. Ionization is generally adverse to adsorption by carbon as strongly-ionized materials are poorly adsorbed. Hydrogen ions, which are significantly adsorbed under some conditions, would be an exception to this. Some negative ions, therefore, are more sorbable when associated with hydrogen ions. For this reason, mineral acids - such as sulfuric acid - are sorbable at higher concentrations.

A change in ionization can drastically affect adsorption. A low pH, for example, promotes the adsorption of organic acids whereas a high pH would favor the adsorption of organic bases. Phenol adsorbs strongly at neutral or low pH while the adsorption of the phenolate salt at a high pH is poor. The optimum pH is therefore solute-specific and must be determined for each wastewater.

Temperature. As adsorption reactions are generally exothermic and high temperatures usually slow or retard the adsorption process, lower temperatures have been reported to favor adsorption (1,5). Very little information has been presented, however, which documents significant shifts in adsorbability within the temperature range of 65°F to 90°F (typical of most wastewaters). Lower temperatures should increase adsorption, but the effect in aqueous solutions is very small.

Adsorption of Mixed Solutes. Most wastewaters contain a myriad of compounds which may mutually enhance, interfere, or act independently in the adsorption process. Factors which affect overall adsorption of multiple adsorbates include the relative molecular size and configuration, the relative adsorptive affinities, and the relative concentrations of the solutes (1). Predictive models obviously require validation for complex wastewaters, as extrapolation from investigations using synthesized wastes containing controlled concentrations of selected adsorbates may not reflect all of the interactions occurring in the waste.

A summary of the factors which potentially influence adsorbability is presented in Table 4.

PROPERTIES OF ACTIVATED CARBON

Activated carbons are made from a variety of materials including weed, peat, lignin, bituminous coal, lignite, and petroleum residues. Granular carbons produced from medium volatile bituminous coal or lignite have been most widely applied in the treatment of wastewater as they are relatively inexpensive and readily available. The activation of carbon is essentially a two-phase process which includes burning off the amorphous decomposition products and enlarging the pores in the carbonized material (6). The burn-off, or carbonization, phase involves drying the carbon at approximately 170°C, heating the material to 270°C to 280°C with the evolution of carbon monoxide, carbon dioxide, and acetic acid, and, finally, completing the carbonization process at a temperature of 400°C to 600°C. The yield following carbonization is approximately 80 percent. The intermediate product is then activated by using carbon dioxide or steam at a temperature of 750°C to 950°C, burning off decomposition products, exposing and widening the pores in the development of macroporous structure. In the activation process, the kind of adsorptive powers developed are determined by:

1. the chemical nature and concentration of the oxidizing gas;
2. the extent to which the activation is conducted;
3. the temperature of the reaction; and
4. the amount and kind of mineral ingredients in the char (5).

The proper activation conditions provide an oxidation which selectively erodes the surface so as to increase the surface area, develop greater porosity, and leave the remaining atoms arranged in configurations that have specific affinities.

Activated carbons from coke, coal, or lignite have specific properties, depending on the material source and the mode of activation. Property standards are therefore helpful in specifying carbons to perform a specific task.

As a rule, granular carbons made from calcined petroleum coke have the smallest pore size, the largest surface area, and the highest bulk density. Lignite carbon has the largest pore size, least surface area, and the lowest bulk density. Bituminous coal has a bulk density equal to that of petroleum coke and an average pore size and surface area somewhere between those of petroleum coke and lignite-based carbons (7). A brief description of carbon properties follows:

Total Surface Area: This is the surface area of carbon expressed in square meters per gram, normally measured by the adsorption of nitrogen gas by the BET method (8).

Carbon Density: Apparent density is the weight in grams of one ml of carbon in air. Bulk density, backwashed and drained, is often used and is usually expressed in pounds per cubic foot.

Particle Size Distribution: The particle size distribution is critical in terms of hydraulic loading and backwash rates. Commonly manufactured particle size ranges for granular activated carbons expressed in limiting U.S. Standard Sieve Sizes include 8 x 16, 8 x 30, 10 x 30, 12 x 40, and 20 x 40. Effective sizes (sieve opening at which 10 percent of the material passes) range from 0.55 mm to 1.30 mm. In general, the uniformity coefficient (the millimeter opening at which 60 percent of the material passes divided by the millimeter opening at which 10 percent of the material passes) for granular activated carbon should not exceed 2.1.

Adsorptive Capacity: The best measure of adsorptive capacity is the effectiveness of the carbon in removing the critical constituents (BOD, COD, color, etc.) from the wastewater in question. Various tests, however, have been developed to give relative removal capacities of activated carbon under specific conditions. Phenol number is used as an index of a carbon's ability to remove taste and odor compounds; tannin is representative of organic compounds added to water by decayed vegetation; and iodine and molasses numbers are used to show if a carbon is activated. The iodine number, defined as the milligrams of iodine adsorbed by one gram of carbon (with an iodine concentration in the residual filtrate is 0.03) is probably the most widely used method of expressing carbon capacities. It generally can be correlated to the ability of an activated carbon to adsorb low molecular weight substances while the molasses number correlates the carbon's ability to adsorb higher molecular weight substances. The iodine number measures the micropores having an effective radius of less than 20 angstroms and the molasses number measures the transitional pores ranging from 20 to 500 angstroms.

These are the principal general parameters used in specifying carbons, the objective being the selected carbon

1. has the adsorption capability to meet the effluent requirements;
2. incurs minimal losses occurring during carbon transport and regeneration;
3. has good hydraulic characteristics with respect to head loss or pressure drop; and
4. represents the most cost-effective media to accomplish the prescribed task.

These, of course, represent general parameters of specification and should be augmented by test data and process requirements developed from bench- or pilot-scale evaluation using representative wastewater samples and selected carbons.

Comparative properties of the most widely used carbons in wastewater treatment - those from lignite and bituminous coals - are shown in Table 5 (6); a broader presentation of properties from commercial carbon manufacturers also is tabulated in this Table (9). Typical properties of a petroleum-base powdered carbon developed but not yet marketed by AMOCO are shown in Table 6.

REGENERATION

Because of economic and solid waste disposal considerations, it is generally more feasible to regenerate spent carbon for subsequent reuse than to dispose of it. In the regeneration process, the objective is to remove from the carbon porous structure the previously-adsorbed materials, thus reinstituting its ability to adsorb impurities. There are several modes of regeneration which can be applied including thermal, steam treatment, solvent extraction, acid or base treatment, and chemical oxidation. Of these, only thermal regeneration using a multiple-hearth or rotary-tube furnace is widely applied in wastewater treatment. The discussion on regeneration therefore centers around thermal treatment.

Thermal regeneration refers to the process of drying, thermal desorption, and high temperature (1,200°F to 1,800°F) heat treatment in the presence of limited quantities of oxidizing gases such as water vapor, flue gas, and oxygen (10). Multiple-hearth furnaces are the most commonly used, although rotary kilns or fluidized-bed furnaces are occasionally applied.

The sequential stages in thermal regeneration are shown in Table 7. Of these steps, the gasification stage is the most critical. The system should be controlled in order to selectively gasify the sorbed organic material while minimizing the gasification of the carbon structure. Basically, there are three major variables involved in thermal regeneration. These include furnace temperature, residence time, and the carbon loading. Of these three, furnace temperature is controllable, although it may take several hours to adjust, the residence time can be changed by varying the rabble-arm speed in a multiple-hearth furnace, or the rotation rate and slope of the tube in a rotary kiln. Very little can be done to change the carbon loading, which affects the severity of regeneration required.

The multiple-hearth furnace is the most commonly used system for granular carbon regeneration. A schematic diagram of a typically-designed multiple-hearth furnace is shown in Figure 3. The wet spent carbon is added at the top of the furnace and drops from hearth to hearth, being raked along by the rabble arms. The temperatures shown for the various hearths are typical gas temperatures for granular carbon regeneration. It was found that the addition of steam on hearths four and six gave a more uniform distribution of temperatures throughout the furnace. The effect of steam is to reduce the apparent density and increase the iodine number of the regenerated carbon (6). Normally, about one pound of steam per pound of carbon is used. Natural gas or fuel oil is usually added to supply the auxiliary heat. Although the fuel requirement varies, generally about 3,000 BTU/lb of carbon and 1,300 BTU/lb of steam generated is required.

Rotary kiln furnaces are not being installed in new facilities but many are still in use. The kilns are usually direct-fired, counter-current units with steam injection with up to 10 percent excess air. Again, natural gas or fuel oil is commonly used as auxiliary fuel. The heat efficiency of rotary kilns is less than that of multiple-hearths.

Fluidized-bed systems for powdered carbon regeneration have been evaluated on a pilot scale and appear to have promise (11, 12, 13). In this process a bed of inert granular material such as sand is fluidized by the upward flow of hot gases and the wet spent carbon is injected directly into the bed. The inert bed particles provide a reservoir of heat which is rapidly transferred to the spent carbon particles. The heat economy of the fluidized-bed furnace is less favorable than the multiple-hearth furnace or the rotary kiln - providing afterburners are not required.

There is considerable debate as to the effect of regeneration on carbon capacity, carbon losses during the regeneration cycle, and hydraulic characteristics of the regenerated carbon. Much of this is focused on the regeneration effects on lignite as compared to bituminous carbon. The manufacturers of lignite claim that, after a number of regeneration cycles, both carbons tend to become more like each other and perform the same (9). Specifically, lignite - while softer and lighter than bituminous - is less susceptible to change during regeneration and can be regenerated under less severe conditions (lower temperature and shorter residence time). The bituminous manufacturers note that lignite carbon losses per cycle are higher than bituminous, indicating a higher operating cost, and bituminous adsorption capacities based on molecular weights ranging from phenol at 94 to dextran at 10,000 are significantly higher than lignite (14). It is not the intent in this writing to favor one over the other, but simply to present information from manufacturers of both types. Based on discussions with independent evaluators of bituminous and lignite, several trends in thinking evolve. First, few full-scale plants using lignite are currently in operation, necessitating an evaluation based on pilot-plant studies. There appears to be little firm evidence that bituminous carbon capacities are higher than those of lignite, although screening tests should be conducted in any event to determine the optimum carbon to perform a specific task. Somewhat higher losses have been noted during regeneration of lignite as compared to bituminous (six to nine percent for lignite, and four to seven percent for bituminous over three cycles). Lignite requires lower temperature for its regeneration and more skilled regeneration operation and control. There has been little evidence to show significant hydraulic differences as demonstrated by head loss characteristics in the two carbons following regeneration. Carbon selection is therefore predicated on process test results, capital cost requirements, and an annualized cost evaluation.

EXPERIENCE IN CARBON TREATMENT OF MUNICIPAL WASTEWATERS

Treatment of municipal wastewaters using activated carbon has been practiced on a full scale for over 10 years. For this reason, ample performance records are presently available for a realistic evaluation of this application, both in the physical/chemical and biological effluent polishing modes of treatment. A summary of these systems has been tabulated elsewhere, but it is the intent in this section to document selected municipal facilities and discuss salient features of these systems which are pertinent to this overall discussion on carbon. The two effluent polishing systems selected for discussion are the South Lake Tahoe and Colorado Springs facilities. The physical/chemical discussion centers around the new plant being constructed for the Cleveland Regional Sewer District, with the Garland, Texas; Rosemount, Minnesota; and Pomona, California plants also included. A syllabus of these selected case histories is presented as follows.

South Tahoe Tertiary Treatment System. The first major and most widely publicized application of activated carbon in treating domestic wastewater was the system constructed for the South Tahoe Public Utility District in 1965. The plant was conceived to polish the effluent from an existing activated sludge facility to a quality level which would have little or no impact on the receiving waters in an ecologically-sensitive area.

The facility consists of a chemical mix-coagulation, precipitation, and clarification unit, an ammonia stripping tower (which has been used infrequently), a recarbonation and settling basin, mixed-media filters, carbon adsorption, and final chlorination. A simplified flow diagram is shown in Figure 4 (15). The water quality at various points in the process following 18 months of operation is presented in Table 8 (16). The more recently reported water quality at the various stages of treatment is presented in Table 9 (9). The carbon (bituminous) efficiency per regeneration period at the South Tahoe Plant is cited in Table 10 (6).

It should be recognized that this facility was a demonstration project, involving expensive capital and annual expenditures. With the possible exception of nitrogen, the effluent quality should represent the best level obtainable in treating a domestic wastewater effectively using maximum biological treatment polished by chemical treatment, filtration, and carbon adsorption.

Colorado Springs Tertiary Treatment System. As at Tahoe, the Colorado Springs treatment system involves chemical treatment, filtration, and carbon adsorption for polishing a slipstream of biologically treated effluent. There are basically two regimes of historical data from this facility. The first was when the slipstream was taken from an overloaded trickling filter effluent (the flow diagram schematically illustrated in Figure 5). The second regime follows the addition of a contact stabilization facility to the biological treating component of the system. This indicates that the influent to the polishing portion of the system, the design data for which are presented in Table 11, has a lower concentration of biodegradable organics in the second regime than in the first (17). This is detected in a general comparison of the effluent quality observed during the two periods. Effluent quality data from a three-month period in 1972 indicate an approximate level obtained during the first regime. The average quality values for the reactor-clarifier influent and effluent, filter effluent, lead carbon column effluent, and polishing carbon effluent are tabulated in Table 12. The data averaged during the second regime of operation are shown in Table 13 (17). Considerable improvement is noted in the comparison, underscoring the need for adequate biological pretreatment if the tertiary system is to realize maximum performance. It is noted that the Tahoe and Colorado Springs (second regime) effluents are relatively similar - both plants have adequate biological pretreatment. The deterioration of effluent quality when this is not the case is evidenced in Table 12.

The Colorado Springs facility is using a bituminous coal activated carbon, using a multiple-hearth furnace regeneration system. As in the other carbon systems, there has been sulfide generation problems in the carbon vessel. This problem has been ameliorated by adding a copper sulfate solution (100 mg/l as $CuSO_4$) to the top of the carbon columns and altering the backwashing frequence to remove biological solids.

Cleveland Regional Sewer District Physical/Chemical System. A physical/chemical wastewater treatment plant of which activated carbon is an integral part is presently being constructed for the Cleveland Regional Sewer District (CRSD) at the Cleveland Westerly plant site. This system is designed to receive an average flow of 50 $\bar{M}$GD with peak flows of 100 $\bar{M}$GD. A flow diagram of this system is shown in Figure 6. Extensive pilot-plant treatability studies were conducted prior to finalizing the design as there is a significant industrial contribution in the raw waste load (18). Moreover, assurance of meeting the NPDES requirements of 20 mg/l BOD (30-day average) and 30 mg/l (seven-day average) was required. These studies, combined with those more recently conducted by CRSD, provided some interesting results with respect to carbon adsorption.

The raw waste load of the Westerly collection system documented during the two pilot studies (1970-71 and 1974-75) is shown in Table 14. The strength of this wastewater, combined with the organic nature of the industrial component, created some difficulty in meeting the required permit levels during the pilot-plant evaluation. Although these results could be overly-pessimistic for various reasons, CRSD evaluated several process alterations with the objective of improving process efficiency and effluent quality. Most of this investigation centered around the use of ozone injection - both as a post-carbon and as a precarbon mode of operation. The postozonation step was originally conceived as strictly a disinfection step, although some further reduction of BOD through ozone oxidation was anticipated. However, studies indicated the ozone requirement for disinfection to the required level of 200 fecal coliforms per 100 ml ranged from 2.6 to 10.9 mg/l (19). The higher doses were attributed to the ozone demand from the sulfides generated in the carbon columns and ferrous bicarbonate resulting from iron slugs in the influent. This ferrous species was solubilized in the recarbonation step and was not altered while passing through the carbon columns. As the higher demands of ozone are economically prohibitive, reducing the ozone-demanding constituents or looking closer at chlorine was merited. Moreover, postozonation did not improve organic effluent quality - as indicated in Table 15. Ozonation prior to the carbon columns was then applied by CRSD with encouraging results. This quality improvement in terms of a frequency analysis of carbon column effluent BOD is shown in Figure 7. The same trend in terms of COD is shown in Figure 8. These results infer that some nonsorbable compounds are converted to more sorbable intermediates through ozone transformations. This possibility is substantiated in the literature, documenting ozone oxidation of aldehydes, ketones, and alcohols to carboxylic acids, the product being more sorbable than the reactants (20, 21). Based on these results, the possibility of injecting ozone prior to the carbon columns is being seriously considered because of the potential advantages of:

1. possibly transforming nonsorbable compounds to sorbable compounds, enhancing carbon adsorption efficiency;
2. reducing the bacterial load to the carbon columns through particle sterilization; and
3. increasing the dissolved oxygen level in the carbon column influent, reducing the possibility of sulfide production and anaerobic bacterial activity.

There may be problems concerning this approach, such as the technical problems involved with injecting ozone in the pressurized carbon influent line, the high decomposition rate of ozone, and enhancing corrosion potential in the carbon reactors. Moreover, disinfection following carbon adsorption still needs to be resolved. However, the advantages presently appear to outweigh the disadvantages and this approach is being seriously considered as a process modification.

Garland Physical/Chemical System. A physical/chemical treatment plant is presently being constructed at Garland, Texas. This 30 $\bar{M}$GD plant is being designed to produce an effluent having less than 10 mg/l BOD and TSS. The raw wastewater quality used for design is presented in Table 16 (22). The flow diagram for this facility is shown in Figure 9. The carbon basins are common-wall concrete facilities, each having a surface area of 950 square feet and a depth of 10 feet. Nine basins can treat the 30 $\bar{M}$GD, while the remaining basin is off-line for the backwashing or regeneration. The wastewater is in contact with the carbon for a minimum of 30 minutes and the upflow rate is 2.5 gpm/ft^2 at design flow. A 14.5 foot multiple-hearth furnace is designed to regenerate 80,000 pounds of carbon daily. Based on the treatability studies, an effluent quality of 15 mg/l COD and 10 mg/l BOD is predicted (22).

Rosemount Physical/Chemical System. The Rosemount, Minnesota physical/chemical facility has been in operation since 1974. The system receives between 0.3 and 0.6 $\bar{M}$GD and consists of screening, chemical clarification using either lime or ferric chloride, prefiltration, upflow activated carbon adsorption, postfiltration, clinoptilolite ammonia exchangers, and disinfection. During the first year of operation, the average BOD removal was 90 percent, the average effluent BOD concentration being 23 mg/l. More recently, however, operating problems have been reduced and the reported effluent BOD has been in the range of five to 10 mg/l (23).

Pomona Physical/Chemical Pilot Plant. A pilot-scale physical/chemical system has been operating for 27 months in Pomona, California, under the auspices of the Los Angeles County Sanitation District and the Environmental Protection Agency. The objectives of this study included an evaluation of the long-term effectiveness of granular activated carbon in the removal of soluble organic matter from chemically-clarified municipal wastewater, controlling hydrogen sulfide generation in the carbon columns, and determining the effects of repeated thermal generations on carbon characteristics and performance.

A flow diagram of the pilot system is shown in Figure 10, the design data for which are presented in Table 17 (24). The primary organic control parameters used in these studies were total chemical oxygen demand (TCOD) and the dissolved chemical oxygen demand (DCOD). A summary of the overall performance of the physical/chemical system is presented in Table 18. These quality levels represent average values observed during the 27 months of study. For comparative purposes, the effluent quality from an 8.0 $\overline{\text{M}}$GD activated sludge system treating the same wastewater is also included. As noted in Table 18, the major portion of pollutants, with the exception of DCOD, was removed in the clarification phase.

The problems of excessive biological growths in the columns, particularly the biochemical reduction of sulfates, has persisted in many of the case histories cited. A review of this problem was therefore an integral part of the Pomona study. As microorganisms have the hydrogen acceptor preference of molecular oxygen, nitrate, sulfate, and oxidized organics, it follows that an environment having the presence of sulfates and organics and the absence of molecular oxygen and nitrates would favor the anaerobic sulfate reducers. The sulfide levels in the effluent approached as high as six mg/l. This was a major concern as sulfide production was correlated directly to net head loss in the column (head loss before the daily backwash minus the head loss after backwash). The fact that the column head loss was caused primarily by abundant biological growths in the column is underscored by the graphical relationship depicted in Figure 11 (24). Several methods of ameliorating the biological proliferation and sulfide production were undertaken. This concluded oxygen addition, intensive air/water backwash, chlorination, and sodium nitrate addition to the carbon column at an average dosage of 5.4 mg/l (as N) was determined to be the most effective in terms of retarding sulfide generation in the carbon column.

The spent carbon used in the regeneration studies was backwashed, dewatered to approximately 50 percent moisture, conveyed to a six-hearth furnace, and regenerated at temperatures ranging from 1,650°F to 1,790°F. Steam in the amount of 0.6 lb/lb of carbon was added to the lower two hearths to enhance the regeneration. The regeneration cycle normally took from 53 to 66 hours to complete. The effects of regeneration on the physical properties of the carbon are shown in Table 19 (24). A reduction in the iodine number (a measure of the extent to which the micropores have been cleared) is noted, although the molasses number (a measure of the extent of macropore clearing) is essentially unchanged. The ash content of the carbon, which measures the amount of calcium and other inorganic residues picked up by the carbon during service increased over 60 percent from the virgin level during the first regeneration. The ash increase during the second regeneration was less, however, with a decrease during the third regeneration. The overall carbon regeneration loss (bituminous coal) ranged from 2.5 to 6 percent with an average loss of 4.3 percent over three regenerations.

Summary. A summary of the municipal wastewater treatment using the tertiary applications of activated carbon has been published recently and is shown in Table 20 (6). A similar summary for a straight physical/chemical application of carbon is shown in Table 21 (6) and in Table 22 (25).

EXPERIENCE IN CARBON TREATMENT OF INDUSTRIAL WASTEWATERS

Although ample carbon treatment data from full-scale facilities are becoming available from the municipal sector, much of the performance data in industrial applications evolves from pilot-plant studies. There are several full-scale carbon systems treating industrial wastewaters, however, and this section includes results from pilot studies and selected operational systems. Specifically, results from pilot-plant studies - primarily in the refinery and petrochemical sector - will be cited, as well as the full-scale systems at the ARCO Refinery near Wilmington, California, the Reichhold Chemicals system in Tuscaloosa, Alabama, and the British Petroleum Refinery in Marcus Hook, Pennsylvania.

Pilot Carbon Studies. There have been pilot studies conducted in the industrial sector evaluating activated carbon as both a total (physical/chemical) process and as an effluent polishing (tertiary) unit. Nine of these studies have been conducted by the author for various petrochemical and petroleum refining facilities (26). The efficiency ranged from 50 to 86 percent COD removal, as noted in Table 23. It should be recognized that these results were obtained using virgin carbon with controlled hydraulic and feed rate regimes. The attendant problems of full-scale operation and the effect of using regenerated carbon on process efficiency should be considered when translating these results to what might occur in an operating carbon treatment system.

A comprehensive pilot-plant study treating petroleum refinery effluents by activated carbon was conducted recently by the Environmental Protection Agency (27). Both API separator effluent and biologically-treated effluent were charged to the columns in order to obtain a comparative evaluation. The results of this study in terms of BOD and COD removal are plotted in Figures 12 and 13, respectively. It is apparent that, when operated in parallel, the biological system was more effective in removing BOD and COD - particularly the former. This is consistent with the results observed in pilot studies conducted by the author. It is also noted that carbon adsorption following biological treatment was particularly effective in reducing both the BOD and COD to low levels. The residual COD is in the same range as that cited in Table 23 when the carbon application mode and influent COD levels were similar. The complete results of this study are shown in Table 24. It is noted that there is no removal of cyanides or ammonia although there was a reduction of the cited organic constituents, particularly phenols. There was surprisingly good removal of chromium, copper, iron, and zinc although the exact mechanisms of removal were not determined. The carbon capacity observed in the columns was 0.31 lb TOC removed/lb of carbon, while the isotherm determined capacity was 0.12 lb/lb. This difference was attributed to biological activity observed in the column. The carbon regeneration activity analysis is reported in Table 25, the change in iodine and molasses numbers showing trends similar to those observed in previous studies. The investigators emphasized that these data were generated using virgin carbon in the columns, and cautioned that the presence of iron or aluminum salts present in the effluent could have a deleterious effect on the carbon through the regeneration cycle. They hypothesized that aluminum salts can remain on the surface of the carbon during regeneration, reducing the effective surface area of the carbon and reducing its adsorption capacity. Moreover, iron salts can catalyze oxidation reactions of the carbon and the gases during regeneration, thus permanently damaging the carbon structure (27).

Extensive pilot-plant studies have been conducted recently by Union Carbide evaluating activated carbon as a tertiary process treating effluent from an activated sludge plant receiving petrochemical wastewaters (28). The objectives of this study were both to establish a basis of justification for applying activated carbon and to optimize its design. Controlled organic and hydraulic application rates were applied to pilot-scale carbon columns. The results of the various throughput rates are listed in Table 26. The first verity which can be deducted from this Table is the fact that, as the activated sludge improves in quality, the efficiency of the adsorber in terms of COD or soluble organic carbon (SOC) improves. The improved efficiency with decreasing hydraulic throughput rates is also apparent. There was still a 30 to 50 percent COD residual in the adsorber influent attributable to organic compounds which are neither biologically degradable nor sorbable on activated carbon. There was a high BOD residual at the same throughput rate, although this residual was reduced to 35 to 50 percent of the adsorber influent at the uneconomical throughput rate of 0.15 bed volumes per hour. This BOD residual includes low molecular weight-oxygenated organics such as aldehydes, ketones, alcohols, glycols, and other polar organics which are adsorbed to a very limited extent. Other observations from this study are cited as follows:

1. breakthrough curves for multi-component wastewaters tend to be poorly defined and sporadic rather than sharp sigmoidal wavefronts;
2. in multi-bed series adsorbers, the lead bed removes the more readily-adsorbable organics and has the highest adsorptive capacity - typical capacities through both beds ranged from 0.2 to 0.4 lb COD/lb of carbon and 0.1 to 0.3 lb BOD/lb of carbon (the observed capacities for the first bed generally were twice as high as those observed in the second); and
3. the maximum hydraulic application rate that appeared to be technically justifiable was 0.5 bed volumes per hour (through both columns of the series).

Full-scale Carbon Studies. There are currently several full-scale operational carbon treatment systems in the United States. Three systems from which data are available are cited here. These include the Atlantic Richfield (ARCO) system in California, the Reichhold system in Alabama, and the British Petroleum (BP) system in Pennsylvania.

ARCO Carbon Treatment System (Watson Refinery)

The first full-scale carbon treatment system in the petroleum refining industry was installed by ARCO at their Watson Refinery near Wilmington, California. This facility was necessitated by a resolution from the Los Angeles Regional Water Quality Control Board which limited the amount of COD that could be discharged by industry into the Dominguez Channel in Los Angeles County. At the time, process wastewaters could be treated in the County's primary treatment unit, but they could not accommodate storm runoff from the Refinery. This presented a problem as the storm water collection system and the process sewers were interconnected. Therefore, during periods of rainfall, the combined storm runoff and process flow could not be sent to the County nor could it be discharged to Dominguez Channel because of its COD concentration. A holding basin and a carbon treatment plant were therefore deemed to be the most efficacious way of treating this combined flow on an intermittent basis (29).

The treatment system, completed in 1971, is illustrated schematically in Figure 14. The process wastewater flows through an API separator and then through pH adjustment and chemical flocculation tanks. Following the addition of both coagulants and polyelectrolytes, the flow is routed to one of two circular dissolved air flotation units. At this point, the oil and grease (O & G) levels are normally below 15 to 20 mg/l. Under dry weather conditions, the flow goes to the County for further treatment. During periods of rainfall, it is diverted to a 50 million gallon holding basin where it is surged and conveyed "as required" to the carbon treatment plant. The plant consists of 12 adsorber cells, the flow to which is controlled by a handwheel-operated slide gate. Each bed can be backwashed with treated water from a backwash sump, the backwash water being returned to the holding basin. The carbon handling and regeneration system includes storage hoppers for spent and regenerated carbon, a pump, eductor, piping, and controls to convey the carbon from any cell to the regeneration furnace and back, and the multiple-hearth furnace with gas scrubber. It is gas-fired and supplemental steam and air are added on two hearths. An afterburner section is separately gas-fired to raise the off-gas temperatures to approximately 1,450°F (necessary to combust the organic vapors in the exit gas).

The actual design criteria for the system are presented in Table 27. Based on a probability distribution of two typical runs presented in Figure 15, the effluent COD was in the range of the predicted level if the influent concentration did not exceed the design basis. Chlorination was attempted once the effluent COD exceeded the design level on the premise that the halogenated compounds would be more effectively adsorbed and the overall performance would be enhanced. There was no noticeable improvement in effluent COD when this step was concluded, however (29). Although oil and grease was not cited as a design parameter, the observed effluent concentration and its dependence on the influent level is shown in Figure 16. The performance of this full-scale system in terms of COD removal approximates the design basis and the observed reduction of COD and O & G is consistent with pilot studies using similar wastewaters. It was noted, however, that algal proliferation in the holding basin adversely affected the carbon plant performance. When excessive algal growths developed, a deterioration of effluent quality and more frequent backwashing was characteristic of the system. At one time, the algae became so concentrated that the carbon plant had to be shut down. Copper sulfate was added to the holding basin to minimize algal growth and ease this problem.

The most significant variance of observed performance from the basis of design was the carbon capacity. Although a precise determination was not possible, the loading based on several runs ranged from 0.30 to 0.35 lb COD removed/lb of carbon, rather than the 1.75 lb COD/lb carbon prediction cited in Table 27.

With the exception of carbon capacity, the carbon plant generally performed as expected. It is no longer in operation, however, primarily because the treatment requirements imposed by Los Angeles County have been changed.

Reichhold Carbon Treatment System (Tuscaloosa Plant)

The Reichhold Chemical Plant produces sulfuric acid, formaldehyde, pentaerythritol, sodium sulfate, sodium sulfite, orthophenylphenol, and a number of synthetic resins. A carbon adsorption system was designed to treat an effluent flow of 500,000 gpd having an average BOD concentration of 390 mg/l, a COD level of 650 mg/l, and a pH ranging from 5.4 to 12.3 (30). An agreement between the Company and the Alabama Water Improvement Commission established an organic removal objective of 90 percent.

A physical/chemical treatment plant using activated carbon was designed and constructed and Figure 17 presents a simplified flow diagram. The process streams are routed to a 2.5-day retention equalization basin where the water is pumped to an acid mixing chamber. Concentrated sulfuric acid is added to maintain a pH range of 6.5 to 8.5. A nonionic polymer is added prior to the flocculation chamber. Following gravity sedimentation, the water is pumped to one of two moving-bed adsorbers. Each adsorber contains 124,000 lb of granular activated carbon. At the design flow rate of 175 gpm/adsorber, the empty bed contact time is approximately three hours. Treated water is collected in a trough at the top of each adsorber where it flows to a final retention tank and then to the river. A conventional regeneration furnace with an afterburner and wet scrubber system is used for reactivation of the carbon.

In the first few months of operation, the results have been reported as meeting the effluent quality requirements. The effluent BOD has been in the 35 to 40 mg/l range, while a 90 percent removal of COD infers an effluent at the 65 to 70 mg/l level (30).

British Petroleum Carbon Treatment System (Marcus Hook, Pennsylvania)

The British Petroleum (BP) Refinery is a 105,000 barrel/day Class "B" refinery located in Marcus Hook, Pennsylvania. In order to comply with discharge standards prescribed by the Delaware River Basin Commission (DRBC), a preliminary engineering program and treatability study was undertaken by the Company. Based on these results, the decision to treat the effluent from the existing API separator to the required level using a filtration/carbon adsorption system was made.

The treatment system, placed into operation in March 1973, is shown in Figure 18 (31). The API separator effluent flows to an intermediate surge basin where it is pumped to three downflow filters, operated in parallel. The flow rate ranges from seven to 12 gpm/ft^2, depending on the operation, and the media consists of 2.5 ft of anthracite and 4.5 ft of sand. The filters are backwashed using filtered water, with provisions for air scouring at 7.1 scfm/ft^2. The design filter pressure is 47.5 psi and the maximum allowable pressure drop through the media is 6.5 psi. The backwash interval is 12 hours.

Three carbon adsorbers (10 ft diameter and 65 ft high) are operated in parallel. Each adsorber contains 92,000 pounds of granular activated carbon in a bed depth of 45 feet. An additional 8,000 pounds occupy the lower and upper cone areas. Flow to the three adsorbers is controlled by the level in the filtered water holding tank. The upward flow rate is 8.5 gpm/ft^2, which gives an empty bed contact time of 40 minutes. Spent carbon at the bottom of the adsorber is pulsed out at the rate of approximately 1,000 lb/day. Fresh carbon is then added to the top of the column from a feed hopper. The design criteria and activated carbon properties for the system are shown in Table 28 (32).

The regeneration facility is a five-foot diameter multiple-hearth furnace. The design feed rate to the six-hearth furnace is 125 lb/hr. In an atmosphere controlled by the addition of steam, the adsorbed organics are volatized and oxidized. In order to insure complete oxidation, all flue gases pass through an afterburner fired by refinery fuel gas and maintained at a temperature of 1,350°F. A wet scrubber is included for gas cooling and the removal of particulate matter. The design data for the thermal regeneration system is shown in

Table 29.

As the full-scale system has been in operation for over two years, performance data are available (31, 32). During the first months of operation while the adsorber still contained virgin carbon, the COD removals were determined to be independent of influent concentration but dependent on contact time. This relationship is shown in Figure 19. The oil and grease removal during this period, shown in Figure 20, followed two different regimes. Good removal was observed initially prior to the start of carbon pulsing. However, once the pulsing began, taking the pulsed bed out of operation, the adverse effect on the remaining two columns is reflected in terms of deteriorating effluent quality. The reduction of oil removal with increasing increasing influent concentrations is attributed to both the oil removal mechanism and pulse bed "off-line" mode of operation.

There have been four distinct phases of operation since the carbon system came on line. The first period of data reported herein occurred when virgin carbon was in the adsorbers and the foul water condensate stream from the Fluidized Catalytic Cracking Unit (FCCU) was not yet included in the raw wastewater stream. The second period included the FCCU stream, but virgin carbon was still present in the adsorbers as the wave front had not yet reached the top of the carbon bed. The third period encompassed a time following a complete turnover of the carbon bed and still included the FCCU stream. The fourth period excluded this stream and incorporated a modification to the column septum design, still following a complete carbon turnover. The average and maximum adsorber effluent concentrations for several parameters observed during each period is tabulated in Table 30. A significant deterioration in quality following the inclusion of the FCCU foul water condensate and complete carbon turnover in the reactor is noted in Figure 21. This has been attributed to inadequate pretreatment of the API separator effluent in terms of O & G and soluble organic removal as well as significant buildups of anaerobic biological growths and oily materials in the carbon media. A 40 percent decrease in adsorptive capacity of the regenerated carbon also has been observed. The iodine number of the regenerated carbon is 560 to 680, while the virgin carbon was in the range of 950 to 1,000 and the molasses number of the regenerated carbon was 280, or approximately 50 higher than the virgin carbon. This indicates a decrease in micropores and an increase in macropores during the regeneration cycle.

The Company is currently reviewing methods of improving process performance over that observed in the last three periods of operation, or possibly changing the system concept altogether. Particular emphasis is being placed on more adequate pretreatment, including biological oxidation, as steps necessary to effectively use the existing carbon system.

SUMMARY

Activated carbon treatment of industrial wastes, while promising, must be carefully evaluated before process decisions are made and capital funds are committed. As noted in the pilot- and full-scale case histories presented herein, breakthrough geometry and adsorption kinetics of multi-component wastewaters are difficult to define, many organic compounds are not amenable to carbon adsorption, and the effects of regeneration on carbon capacities are variable and unpredictable. For these and other reasons, comprehensive testing and technical reviews are a necessary prerequisite to process commitment.

Unfortunately, most of the literature regarding carbon treatment of industrial wastewaters centers around pilot-plant results. There are, however, sufficient data from pilot studies and the two full-scale systems in the petroleum refinery industry to draw general conclusions, at least within this industrial category. For example, a distribution of long-term average COD concentrations in effluents from carbon adsorbers treating refinery wastewaters is presented in Figure 22 (33). These levels are relatively consistent with those residuals reported in the petrochemical industry (28). A similar presentation of oil and grease effluent levels from a full-scale refinery carbon system is shown in Figure 23. Carbon adsorption capacities in terms of lbs of COD removed/lb of carbon exhausted have ranges from 0.2 to 0.4 in the petrochemical industry and from less than 0.1 to 0.55 in the petroleum refining industry. These are lower than reported carbon capacities for municipal wastewaters, as shown in Figure 24, emphasizing the inaccuracies which can occur by extrapolating results from the treatment of one wastewater and using them as the basis for predicting another.

SYNOPSIS

A review of the current state of the art of activated carbon treatment has been presented. Basic concepts of activated carbon treatment have been included, as well as pertinent municipal and industrial case histories with which the author is familiar. It is recognized that new truths pertaining to this subject become known on a continuing basis. However, in evaluating process concepts, developing design bases, predicting effluent quality, and finalizing management decisions in terms of constructing control systems with attendant capital commitments, one must base these judgments on the current state of the art. It is toward the objective of defining the art of activated carbon treatment that this information is presented.

In the pursuit of this definition, certain apparent verities emerge. Some of the more significant include the following:

1. Adsorption theory is rigorous for single solutes, but becomes less definitive when applied to wastewaters containing multiple components with varying molecular weights and chemical characteristics. A good example is the poorly-defined and erratic breakthrough geometry observed in the carbon treatment of complex industrial wastewaters.
2. Many classes of organic compounds are not amenable to carbon adsorption - particularly oxygenated organics - and show up as residual BOD, COD, or TOC in carbon column effluents. This limits the overall process efficiency of pure physical/chemical treatment systems. As many of these residual compounds are biodegradable, activated carbon as a polishing process is generally capable of producing a better quality of effluent than is the strict physical/chemical application.
3. Anaerobic conditions which prevail in carbon reactors have caused difficulty through the proliferation of biological growths on the carbon media. Sulfide generation has been particularly troublesome. Although biological activity in the column has the potential of increasing carbon capacities and is hypothesized to offer regeneration possibilities, full-scale experience has indicated that uncontrolled biological growth in carbon reactors has more negative features than

positive.

4. Ozonation of wastewaters prior to carbon adsorption has been demonstrated on a pilot scale to enhance adsorption in the columns. This is attributed to the ozone products being more sorbable than the reactants. Other possible attractions of this application are controlling biological densities on the carbon media through partial disinfection and maintaining an aerobic environment in the reactor column.
5. Carbon capacities used as design criteria generally have been overstated and have not been realized in full-scale experience. Breakthrough concentrations which force premature regeneration cycles in single-operated columns, and desorption phenomena which cause low capacities in series-operated polishing columns, are partially responsible for this.
6. Design criteria for carbon adsorption systems should be sensitive to:
   - (a) wastewater constituents and their classification in terms of adsorbability, and the effluent residual potential; and
   - (b) effect of the selected carbon media with respect to capacity, resistance to abrasion, regeneration impacts, and hydraulic characteristics; and
   - (c) the biological growth potential with the associated effects on carbon capacity, backwash requirements, and hydraulic characteristics of the flow through the column; and
   - (d) the necessary pretreatment requirements for control of suspended solids (organic and inorganic), oil and grease, dissolved oxygen, biological population, and other constituents which affect carbon adsorber performance.

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DISCUSSION

Ed Sebesta: Were these pilot plant data taken with regenerated carbon and equilibrated carbon?

Davis Ford: No. It was virgin carbon. That's a good point. Many of the pilot plants studies that we have run have been with virgin carbon. It is not that we don't recognize that it would be more applicable with regenerated carbon, it is just sometimes that it is hard to get that much regenerated carbon from the vendor and that has been our problem. One would think it would be more practical to run all these pilot studies with regenerated carbon.

Bob Huddleston: Do you have any data that indicates whether or not the effects of ozone were anything other than simply killing the microbes?

Davis Ford: Yes. They ran some GC work to identify the nature of the compounds after organization and I don't have the results in this paper. Just in talking with these people, it's what you really have done is gone from the ketones, aldehydes to carboxylic acids, there has been a shift and the carboxylic acids being more ameniable to carbon absorption, so its a combination of the biological growth but also the transformation of these oxygenated organics to carboxylic acids.

M. K. Hutton: Discuss if you will the cost of ozone. Do you have any figures on this? I expect it is quite expensive.

Davis Ford: I left cost completely out of the paper because that is almost another paper itself; but considering the concentration of ozone that we think we have to have, it is probably about 4 or 5 milligrams per liter is within the cost effective parameters that we have set to shis point. So we think it is cost effective.

Anonymous: Do you have some comments on phenol removal?

Davis Ford: No. Phenol is highly sorbable, most of the data we have seen on phenol removal has been excellent and the only exceptions to this was when we just had so many physical problems, the biological growths and oil and grease, that the phenol removal has gone down. I think that is shown in one table. If you don't have this constraint, phenol removal should be good, carbon is a good phenol remover.

Morris Wiley: The little village where I live has a new sewer system and biological treatment plant. It is an extended aeration without any primary treatment, then a second stage nitrification and finally a sand filter. They are able to do less than one part per million BOD and less than one part per million ammonia in the effluent. Now I should caution that it is only operating at one quarter of rated capacity. Thus, it appears that if one has to go to these very low organic and nitrogen contents in the effluent, that one can do it by a conventional biological system simply by spending a lot of money. I estimate that this is about $1,000 per family per year, total annualized cost for this system including the sewer connections which were put in. Have you done any economic studies to try to figure out which would really be preferable, an advanced biological reactor system versus an activated carbon where you need a very low concentration of pollutants in the effluent?

Davis Ford: Let me speak in general terms here. First, you have a good analytical chemist at that plant.

Morris Wiley: Well, I have some reservations about the precision of the tests. The plant operator is a Texaco employee running the plant in his spare time with his wife and his son, but it is a good quality effluent and the county is accepting their test reports.

Davis Ford: Let me say, from the cost studies that we have run, we have seen biological treatment is more cost effective than carbon, I don't think there is any question about that. When you get down to the fact that a biological system can't make a permit and you have to go to carbon, you know some people are not sympathetic with cost effectives, but if you can get to those levels biologically, it just intuitively has to be more cost effective than carbon. Carbon has gone up, it is 50-60¢ now for bituminous. When we started running these studies three or four years ago, it was 32¢ or 30¢ and just because of these lower carbon capacities I have stated, biological treatment has to be more cost effective. If we can make it with biological treatment, that is certainly the theology that I would like to see.

Morris Wiley: Then it looks as though our research should be concentrated on enhancing the effectiveness this biological treatment as Jim Grutsch pointed out earlier?

Davis Ford: I do not disagree with that. I also think we have got to be realistic, there are certain limitations to biological treatment. When you look at BAT, if and when it comes, it is going to take some real engineering to make those numbers biologically.

Neale Fugate: Do you have any data on the possible adsorption of heavy metals, or conversely desorption of heavy metals on carbon?

Davis Ford: Yes, sir. I have it, but it is not presented in the paper. I have just seen some data on that. There is slight reductions of some of the metallic ions probably as metallic hydroxides. I think in some literature absorption of some metallic ions has been reported. It has not been significant, something like 10-15% reduction of zinc, mercury, cadmium, some of these substances but percent removal is quite low, but some removal has been noted. I am not sure of the mechanism as a physical removal of zinc or sorption of zinc iron, but one of those two mechanisms.

Robert L. Wortman: It is my understanding that ozone is a very effective phenol remover, it removes the phenol quite effectively, it is probably even better than activated carbon (through oxidation). It would seem to me that may be secondary conventional treatment followed by ozonation may be as effective as secondary treatment followed by carbonation. My question is, have you had any experience on this in combination with carbon filtration and I am interested in treating each one individually, that is considering ozonization as a treatment method?

Davis Ford: Let me answer that two ways. First of all, I think I mentioned in the talk that we tried preozonation after carbon with bad results. However, there is a treatment plant, financed in part by EPA which goes on line in about two months and that is at Estes Park, Colorado, which is exactly the system you described. Other than that plant, I am not personally familiar with a real good biological treatment system including nitrification followed by ozone but that system is designed that way. That is the upper sanitation district in Estes Park, Colorado, the plant is completed and is probably going through shake down right now and we will get some good full scale information from that facility in the next few months.

Anonymous: I think there is also some work being done in Pomona, I don't know exactly what it was, but on a different combination of ozonation and various schemes; but to further explore the Estes Park, if you say you had a multimedia filter and then go in ozonation, this may be quite effective to work with.

Fred Gowdy: Davis, I wonder if you would give us some of the reasons you believe why the carbon capacities that we have realized in some of our full scale plants, haven't been anywhere close to those predicted by various pilot studies?

Davis Ford: I am not really sure that I know the answer to that, I can just hypothesize. First of all, I think Union Carbide has presented carbon capacities in lead columns as far as polishing columns were concerned, so that would indicate the operation has a lot to do with carbon capacity, in other words, how well you can operate the carbon utilization in a series mode of operation to get the operable capacity of the overall system. You can pretty well do that in a pilot scale. I am not sure you can do it in a full scale quite so easily. It is easier to operate that pilot scale, I assure you, than a full-scale plant. So I think part of the answer lies in the operation. Secondly, it is possible that you had more physical problems in terms of biological growth, influent constituents in the full scale that you don't perceive in a pilot scale. You might control the pilot scale a little better and for this reason are able to realize a better carbon capacity. Those are the two main reasons I think, I just can't prove it.

Ed Sager: I wondered if you would like to elaborate on the back washing features of these columns. Why is that required if you have adequate pretreatment, are you removing suspended solids build-up?

Davis Ford: I think the best case history to point to there is the BP, they have got some data on their filters, good filters which work quite well; but the effluent suspended solids are probably in the 10-15-20 milligram per liter range and these influent suspended solids to the carbon column are going to accumulate after a certain period of time, combined with the biological proliferation in the columns. I think you always have to have the flexibility operational flexibility of back washing columns as well as the filters. I think that has been the experience to date. You may not have to do it, but it is an operational flexibility that you should have. It seems like even if you go in with zero suspended solids, some point in time you are going to have to back wash the filters or the carbon columns.

Pat DeJohn: One of the things that one of the gentlemen asked about the loadings, most of the loadings that are reported are reported with virgin carbon and the properties of activated carbon change quite substantially when you regenerate carbon and I think that is part of the BP problem, they are not able to maintain their phenol standards because of the loss in capacity, adsorptive capacity and consequently, their system has been substantially under design. The other thing that you mentioned about why you should be back washing, that BP plant is a pulse bed unit and there are fines that are created due to the regeneration of the carbon and they have no way to remove those fines; consequently they recycle them back into the absorber and they pulse that unit a lot of times because of pressure drop problems and that is another thing about that particular plant.

Davis Ford: I agree with that. In the past, Pat, when we have had to use virgin carbon, we have just applied a factor on the capacity, reduced capacity, just an empirical factor and that is a less favorable way of doing it than using regenerated carbon; but we just haven't had that luxury a lot of times.

J. J. Chavez: I was just wondering if you could elaborate on the regeneration phase from the economic side by which a refinery could put in one regulation facility and the options open to him if he can't afford one?

Davis Ford: There again I didn't really get into cost. I believe the reported regeneration cost now is something like 15-20¢ per pound. Some manufacturers, I believe, are offering a regeneration service. If you have a small system, it doesn't make sense because of economy in scale to put in your own regeneration facility, to have a contractor regenerate it, if that's possible, but I think if you go into regeneration which in most areas you would have to for most size of plants, you have to count on about a 15-20¢ per pound regeneration cost.

BIOGRAPHY

Davis L. Ford holds a B.S. in Civil Engineering from Texas A & M University and M.S. and Ph.D. degrees in Environmental Health Engineering from the University of Texas at Austin. Dr. Ford is currently Senior Vice President and Member of the Board of Directors of Engineering Science, Inc., in Austin, Texas. Dr. Ford has written 4 books, 20 reports, 60 publications in the field of environmental engineering and has consulted for over 50 industries, the United Nations (WHO and PAHO), the EPA and various state and municipal agencies.

TABLE 1 "COMPARATIVE ANALYSIS OF BATCH ISOTHERM DATA - REFINERY & PETROCHEMICAL WASTEWATERS"

	K	n
OIL SEPARATOR (PRIMARY) EFFLUENT		
Refinery - Petrochemical Complex No. 1	0.0290	0.77
Refinery - Petrochemical Complex No. 2	0.0036	0.80
Refinery No. 3	0.0140	0.36
SECONDARY (ACTIVATED SLUDGE) EFFLUENT		
Refinery - Petrochemical Complex No. 1	0.0062	0.60
Refinery No. 3	0.0043	1.00
Refinery Secondary Effluent	0.0051	0.96
Refinery Secondary Effluent	0.0038	1.08
Refinery Secondary Effluent	0.0020	0.69
SINGLE ADSORBATE		
Phenol	0.1110	5.80
Dichlorethane (pH 4)	0.0045	1.82
(pH 6)	0.0038	1.67
(pH 10)	0.0041	1.49

TABLE 2

AMENABILITY OF TYPICAL ORGANIC COMPOUNDS TO ACTIVATED CARBON ADSORPTION [4]

Compound	Molecular Weight	Aqueous Solubility (%)	Concentration (mg/l) Initial (C_0)	Concentration (mg/l) Final (C_f)	Adsorbability* g compound/ g carbon	Adsorbability* Percent Reduction
Alcohols						
Methanol	32.0	∞	1,000	964	0.007	3.6
Ethanol	46.1	∞	1,000	901	0.020	10.0
Propanol	60.1	∞	1,000	811	0.038	18.9
Butanol	74.1	7.7	1,000	466	0.107	53.4
n Amyl alcohol	88.2	1.7	1,000	282	0.155	71.8
n Hexanol	102.2	0.58	1,000	45	0.191	95.5
Isopropanol	60.1	∞	1,000	874	0.025	12.6
Allyl alcohol	58.1	∞	1,010	789	0.024	21.9
Isobutanol	74.1	8.5	1,000	581	0.084	41.9
t Butanol	74.1	∞	1,000	705	0.059	29.5
2 Ethyl butanol	102.2	0.43	1,000	145	0.170	85.5
2 Ethyl hexanol	130.2	0.07	700	10	0.138	98.5
Aldehydes						
Formaldehyde	30.0	∞	1,000	908	0.018	9.2
Acetaldehyde	44.1	∞	1,000	881	0.022	11.9
Propionaldehyde	58.1	22	1,000	723	0.057	27.7
Butyraldehyde	72.1	7.1	1,000	472	0.106	52.8
Acrolein	56.1	20.6	1,000	694	0.061	30.6
Crotonaldehyde	70.1	15.5	1,000	544	0.092	45.6
Benzaldehyde	106.1	0.33	1,000	60	0.188	94.0
Paraldehyde	132.2	10.5	1,000	261	0.148	73.9
Amines						
Di N Propylamine	101.2	∞	1,000	198	0.174	80.2
Butylamine	73.1	∞	1,000	480	0.103	52.0
Di N Butylamine	129.3	∞	1,000	130	0.174	87.0
Allylamine	57.1	∞	1,000	686	0.063	31.4
Ethylenediamine	60.1	∞	1,000	893	0.021	10.7
Diethylenetriamine	103.2	∞	1,000	706	0.062	29.4
Monethanolamine	61.1	∞	1,012	939	0.015	7.2
Diethanolamine	105.1	95.4	996	722	0.057	27.5
Triethanolamine	149.1	∞	1,000	670	0.067	33.0
Monoisopropanolamine	75.1	∞	1,000	800	0.040	20.0
Diisopropanolamine	133.2	87	1,000	543	0.091	45.7
Pyridines & Morpholines						
Pyridine	79.1	∞	1,000	527	0.095	47.3
2 Methyl 5 Ethyl pyridine	121.2	sl sol	1,000	107	0.179	89.3
N Methyl morpholine	101.2	∞	1,000	575	0.085	42.5
N Ethyl morpholine	115.2	∞	1,000	467	0.107	53.3
Aromatics						
Benzene	78.1	0.07	416	21	0.080	95.0
Toluene	92.1	0.047	317	66	0.050	79.2
Ethyl benzene	106.2	0.02	115	18	0.019	84.3
Phenol	94	6.7	1,000	194	0.161	80.6
Hydroquinone	110.1	6.0	1,000	167	0.167	83.3
Aniline	93.1	3.4	1,000	251	0.150	74.9
Styrene	104.2	0.03	180	18	0.028	88.8
Nitrobenzene	123.1	0.19	1,023	44	0.196	95.6
Esters						
Methyl acetate	74.1	31.9	1,030	760	0.054	26.2
Ethyl acetate	88.1	8.7	1,000	495	0.100	50.5
Propyl acetate	102.1	2	1,000	248	0.149	75.2
Butyl acetate	116.2	0.68	1,000	154	0.169	84.6
Primary amyl acetate	130.2	0.2	985	119	0.175	88.0
Esters						
Isopropyl acetate	102.1	2.9	1,000	319	0.137	68.1
Isobutyl acetate	116.2	0.63	1,000	180	0.164	82.0
Vinyl acetate	86.1	2.8	1,000	357	0.129	64.3
Ethylene glycol monoethyl ether acetate	132.2	22.9	1,000	342	0.132	65.8
Ethyl acrylate	100.1	2.0	1,015	226	0.157	77.7
Butyl acrylate	128.2	0.2	1,000	43	0.193	95.9
Ethers						
Isopropyl ether	102.2	1.2	1,023	203	0.162	80.0
Butyl ether	130.2	0.03	197	nil	0.039	100.0
Dichloroisopropyl ether	171.1	0.17	1,008	nil	0.200	100.0
Glycols & Glycol Ethers						
Ethylene glycol	62.1	∞	1,000	932	0.0136	6.8
Diethylene glycol	106.1	∞	1,000	738	0.053	26.2
Triethylene glycol	150.2	∞	1,000	477	0.105	52.3
Tetraethylene glycol	194.2	∞	1,000	419	0.116	58.1
Propylene glycol	76.1	∞	1,000	884	0.024	11.6
Dipropylene glycol	134.2	∞	1,000	835	0.033	16.5
Hexylene glycol	118.2	∞	1,000	386	0.122	61.4
Ethylene glycol monomethyl ether	76.1	∞	1,024	886	0.028	13.5
Ethylene glycol monoethyl ether	90.1	∞	1,022	705	0.063	31.0
Ethylene glycol monobutyl ether	118.2	∞	1,000	441	0.112	55.9
Ethylene glycol monohexyl ether	146.2	0.99	975	126	0.170	87.1
Diethylene glycol monoethyl ether	134.2	∞	1,010	570	0.087	43.6
Diethylene glycol monobutyl ether	162.2	∞	1,000	173	0.166	82.7
Ethoxytriglycol	178.2	∞	1,000	303	0.139	69.7
Halogenated						
Ethylene dichloride	99.0	0.81	1,000	189	0.163	81.1
Propylene dichloride	113.0	0.30	1,000	71	0.183	92.9
Ketones						
Acetone	58.1	∞	1,000	782	0.043	21.8
Methylethyl ketone	72.1	26.8	1,000	532	0.094	46.8
Methyl propyl ketone	86.1	4.3	1,000	305	0.139	69.5
Methyl butyl ketone	100.2	v sl sol	988	191	0.159	80.7
Methyl isobutyl ketone	100.2	1.9	1,000	152	0.169	84.8
Methyl isoamyl ketone	114.2	0.54	986	146	0.169	85.2
Diisobutyl ketone	142.2	0.05	300	nil	0.060	100.0
Cyclohexanone	98.2	2.5	1,000	332	0.134	66.8
Acetophenone	120.1	0.55	1,000	28	0.194	97.2
Isophorone	138.2	1.2	1,000	34	0.193	96.6
Organic Acids						
Formic acid	46.0	∞	1,000	765	0.047	23.5
Acetic acid	60.1	∞	1,000	760	0.048	24.0
Propionic acid	74.1	∞	1,000	674	0.065	32.6
Butyric acid	88.1	∞	1,000	405	0.119	59.5
Valeric acid	102.1	2.4	1,000	203	0.159	79.7
Caproic acid	116.2	1.1	1,000	30	0.194	97.0
Acrylic acid	72.1	∞	1,000	355	0.129	64.5
Benzoic acid	122.1	0.29	1,000	89	0.183	91.1
Oxides						
Propylene oxide	58.1	40.5	1,000	739	0.052	26.1
Styrene oxide	120.2	0.3	1,000	47	0.190	95.3

Dosage 5 g Carbon C/l solution

TABLE 3 "RELATIVE AMENABILITY TO CARBON ADSORPTION OF TYPICAL PETROCHEMICAL WASTEWATER CONSTITUENTS"

Compound	% Adsorption	Compound	% Adsorption
Ethanol	10	Vinyl acetate	64
Isopropanol	13	Ethyl acrylate	78
Acetaldehyde	12	Ethylene glycol	7
Butyraldehyde	53	Propylene glycol	12
Di-N-propylamine	80	Propylene oxide	26
Monoethanolamine	7	Acetone	22
Pyridine	47	Methyl ethyl ketone	47
2-Methyl 5-ethyl pyridine	89	Methyl isobutyl ketone	85
Benzene	95	Acetic acid	24
Phenol	81	Proprionic acid	33
Nitrobenzene	96	Benzoic acid	91
Ethyl acetate	50		

Initial Compound Concentration = 1,000 mg/l Powdered Carbon Dosage = 5,000 mg/l

TABLE 4 "INFLUENCE OF MOLECULAR STRUCTURE AND OTHER FACTORS OF ADSORBABILITY"

1. An increasing solubility of the solute in the liquid carrier decreases its adsorbability.
2. Branched chains are usually more adsorbable than straight chains. An increasing length of the chain decreases solubility.
3. Substituent groups affect adsorbability:

Substituent Group	Nature of Influence
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule; glyoxylic are more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids.
Double Bonds	Variable effect as with carbonyl.
Halogens	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.
Aromatic Rings	Greatly increases adsorbability.

4. Generally, strong ionized solutions are not as adsorbable as weakly ionized ones; i.e., undissociated molecules are in general preferentially adsorbed.
5. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.
6. Unless the screening action of the carbon pores intervene, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute carbon chemical bonds being formed, making desorption more difficult.
7. Molecules with low polarity are more sorbable than highly polar ones.

TABLE 5

PROPERTIES OF SEVERAL COMMERCIALLY AVAILABLE CARBONS*[6]

	ICI AMERICA HYDRODARCO 3000 (LIGNITE)	CALGON FILTRASORB 300 (8x30) (BITUMINOUS)	WESTVACO NUCHAR WV-L (8x30) (BITUMINOUS)	WITCO 517 (12x30) (BITUMINOUS)
PHYSICAL PROPERTIES				
Surface area, m²/gm (BET)	600-650	950-1050	1000	1050
Apparent density, gm/cc	0.43	0.48	0.48	0.48
Density, backwashed and drained, lb/cu. ft.	22	26	26	30
Real density, gm/cc	2.0	2.1	2.1	2.1
Particle density, gm/cc	1.4 - 1.5	1.3 - 1.4	1.4	0.92
Effective size, mm	0.8 - 0.9	0.8 - 0.9	0.85 - 1.05	0.89
Uniformity coefficient	1.7	1.9 or less	1.8 or less	1.44
Pore volume, cc/gm	0.95	0.85	0.85	0.60
Mean particle diameter, mm	1.6	1.5 - 1.7	1.5 - 1.7	1.2
SPECIFICATIONS				
Sieve size (U.S. std. series)				
Larger than No. 8 (max. %)	8	8	8	—
Larger than No. 12 (max. %)	—	—	—	5
Smaller than No. 30 (max. %)	5	5	5	5
Smaller than No. 40 (max. %)	—	—	—	—
Iodine No.	650	900	950	1000
Abrasion No., minimum	**	70	70	85
Ash (%)	**	8	7.5	0.5
Moisture as packed (max. %)	**	2	2	1

* Other sizes of carbon are available on request from the manufacturers.
** No available data from the manufacturer.
— Not applicable to this size carbon.

TYPICAL PROPERTIES OF 8 X 30-MESH CARBONS[9]

	LIGNITE CARBON	BITUMINOUS COAL CARBON
Total surface area, m²/g	600-650	950-1,050
Iodine number, min	500	950
Bulk density, lb/ft³ backwashed and drained	22	26
Particle density wetted in water, g/cm³	1.3-1.4	1.3-1.4
Pore volume, cm³/g	1.0	0.85
Effective size, mm	0.75-0.90	0.8-0.9
Uniformity coefficient	1.9 or less	1.9 or less
Mean-particle dia., mm	1.5	1.6
Pittsburgh abrasion number	50-60	70-80
Moisture as packed, max.	9%	2%
Molasses RE (relative efficiency)	100-120	40-60
Ash	12-18%	5-8%
Mean-pore radius	33 A	14 A

TABLE 6 "TYPICAL PROPERTIES OF POWDERED ACTIVATED CARBON (PETROLEUM BASE)"

Surface Area (BET m^2/gm)		2,300-2,600
Iodine No.		2,700-3,300
Methylene Blue Adsorption (mg/gm)		400-600
Phenol No.		10-12
Total Organic Carbon Index (TOCI)		400-800
Pore Distribution (Radius Angstrom)		15-60
Average Pore Size (Radius Angstrom)		20-30
Cumulative Pore Volume (cc/gm)		0.1-0.4
Bulk Density (gm/cc)		0.27-0.32
Particle Size	Passes: 100 mesh (wt%)	97-100
	200 mesh (wt%)	93-98
	325 mesh (wt%)	85-95
Ash (wt%)		<1.5
Water Solubles (wt%)		<1.0
pH of Carbon		8-9

TABLE 7 "STAGES OF THERMAL REGENERATION"

Stage	Approximate Temperature (°F)	Processes
Drying	Ambient to 212	Water Evaporation
Thermal Desorption	212 to 500	Physical desorption of volatile adsorbed organics
Pyrolysis and Carbonization	400 to 1,200	Pyrolysis of nonvolatile organics and carbonization of the pyrolysis residue
Gasification	1,200 to 1,900	Gasification of pyrolytic residue through controlled chemical reaction with water vapor, vapor, carbon dioxide, or oxygen

TABLE 8 "WATER QUALITY AT VARIOUS POINTS IN PROCESS" (16)

Quality Parameter		Raw Wastewater	Secondary Effluent	Separation-Bed Effluent	Carbon-Column Effluent
BOD (mg/l)		200-400	20-100	<1	<1
COD (mg/l)		400-600	80-160	20-60	1-25
Total organic carbon (mg/l)		-	-	8-18	1-6
ABS (mg/l)		2.0-4.0	0.4-2.9	0.4-2.9	<0.01-0.5
PO_4 (mg/l as PO_4)		-	25-30	0.1-1	0.1-1
Color (units)		-	-	10-30	<5
Turbidity (units)		-	30-70	<0.5-3	<0.5-1
Nitrogen organic N (mg/l as N)		10-15	4-6	2-4	1-2
Ammonia N (mg/l as N)		25-35	25-32	25-32	25-32
NO_3 and NO_2 (mg/l as N)		0	0	0	0
Unchlorinated:	Coliforms (MPN/100 ml)	-	2,400,000	9,300	11,000
	Fecal coliforms (MPN/100 ml)	-	150,000	930	930
	Virus	-	-	Negative	Negative
Chlorinated:	Coliforms (MPN/100 ml)	-	-	8.6	<2.1
	Fecal coliforms (MPN/100 ml)	-	-	<2.1	<2.1

TABLE 9 "WATER QUALITY AT VARIOUS STAGES OF TREATMENT AT SOUTH LAKE TAHOE"

Quality Parameter	Raw Wastewater	Effluent					
		Primary	Secondary	Chemical Clarifier	Filter	Carbon	Chlorinated Final
BOD (mg/l)	140	100	30		3	1	0.7
COD (mg/l)	280	220	70		25	10	10
SS (mg/l)	230	100	26	10	0	0	0
Turbidity (JTU)	250	150	15	10	0.3	0.3	0.3
MBAS (mg/l)	7	6	2.0		0.5	0.1	0.1
Phosphorus (mg/l)	12	9	6	0.7	0.1	0.1	0.1
Coliform (MPN/100 ml)	50×10^6	15×10^6	2.5×10^6		50	50	< 2

TABLE 10 "CARBON EFFICIENCY PER REGENERATION PERIOD AT SOUTH LAKE TAHOE"
NOVEMBER 1968 THROUGH JANUARY 1971

Parameter		Average	Maximum	Minimum
Carbon Dosage (lb regenerated/million gallons treated)[1]		207	418	111
Iodine Number[2]	Spent Carbon	583	633	497
	Regenerated Carbon	802	852	743
Apparent Density (gm/ml)[2]	Spent Carbon	0.571	0.618	0.544
	Regenerated Carbon	0.487	0.491	0.478
Percent Ash[2]	Spent Carbon	6.4	7.0	5.8
	Regenerated Carbon	6.8	7.2	5.8
Chemical Oxygen Demand	Percent Removal	49.9	63.3	30.1
	lb COD applied	28,250	54,970	15,680
	lb COD applied/$\overline{M}$G	162	254	105
	lb COD removed/$\overline{M}$G	81	149	32
	lb COD applied/lb carbon regenerated[1]	0.78	1.56	0.52
	lb COD removed/lb carbon regenerated[1]	0.39	0.71	0.16
Methylene Blue Active Substances (Methylene Blue Active Substances (MBAS))	Percent removal	77	93	58
	lb MBAS applied	995	1,675	457
	lb MBAS applied/$\overline{M}$G	5.7	10.7	2.6
	lb MBAS removed/$\overline{M}$G	4.4	8.2	1.6
	lb MBAS applied/lb carbon regenerated[1]	0.027	0.045	0.012
	lb MBAS removed/lb carbon regenerated[1]	0.021	0.039	0.007

[1] Based on ft^3 of carbon fed to furnace at 30 lb/ft^3

[2] November 1968 through November 1970

TABLE 11 "COLORADO SPRINGS TERTIARY PLANT DESIGN DATA"

Solid Contact Clarifier	48 ft diameter, 11 ft 9 in sidewall, 2 ft cone depth 1,809 sq ft surface area 168,465 gallon capacity 2 hr detention time and 0.76 gpm/sq ft rise rate - @ 2 $\bar{M}$GD flow
Spent Lime Tank	14 ft diameter, 10 ft sidewall depth, 8 ft cone 1,948 cu ft 14,610 gallon capacity
New Lime Holding Tank	14 ft diameter, 10 ft sidewall depth, 8 ft cone 1,948 cu ft 14,610 gallon capacity
Recarbonization Tank	14 ft diameter, 14 ft sidewall depth, plus 2 ft freeboard - 154 sq ft 2,156 cu ft 16,160 gallon capacity - 12 minutes detention time @ 2 $\bar{M}$GD flow
Activated Carbon Adsorbers	20 ft diameter, 14 ft sidewall depth, 10 ft of carbon media 314 sq ft surface area, 4,396 cu ft 32,970 gallon capacity total tower detention time is 24 minutes - 4.5 gpm/sq ft (@ 2 $\bar{M}$GD flow) carbon bed detention time is 17 minutes - 4.5 gpm/sq ft (@ 2 $\bar{M}$GD flow) 3,140 cu ft of carbon @ 30 lb/cu ft - 94,200 lbs carbon
Dual Media Sand Filters	12 ft diameter, 11 ft sidewall depth, 1 ft 6 in top cone 113 sq ft surface area 1,243 cu ft capacity 9,323 gallon capacity 3 ft of e.s. 1.5 mm sand 5 ft of e.s. 2.8 mm anthrafilt (#2)

TABLE 12 "TERTIARY TREATMENT PLANT DATA SUMMARY (FIRST REGIME)"

PARAMETER	R-C INF.	R-C EFF.	FILTER EFF.	LEAD CARBON EFF.	POLISH CARBON EFF.
BOD	106	46.9	48.0	44.0	33.0
COD	305	120	114	83	64
TOC	76	37.9	36.8	27.9	23.8
TSS	56	31.0	3.7	2.1	3.7
Turbidity	53	10.1	4.2	3.6	3.2
0.PO_4 (total)	32	2.2	1.7	2.2	1.9
0.PO_4 (soluble)	31	0.16	1.6	2.2	1.8
MBAS	5.32	3.22	-	1.36	0.51
pH	7.35	11.44	7.93	6.91	7.12
Alkalinity (total)	197	282	69	63	69
Hardness	163	210	250	240	253
C_a (as C_a^{++})	52	79	95	84	92
C^aC_a (as $^aC_aCO_3$)	130	197	237	209	231
Color	162	44	38	25	13
Sulfates	88	80	439	439	401
Sulfides	0.15	0.14	-	0.26	0.41
Flow (MGD)	1.93	1.93	1.93	1.70	1.70
Lime Dose (ppm Ca 0)		349			

NOTE: During this period, the reactor was operated with a deep sludge blanket of approximately six feet.

TABLE 13 "TERTIARY TREATMENT PLANT DATA SUMMARY (SECOND REGIME)"

PARAMETER	INFLUENT (mg/l)*	EFFLUENT (mg/l)*	REMOVAL (percent)
BOD	102	8.0	92.2
COD	258	15.7	93.9
TSS	62	2.2	96.5
Turbidity	54	2.2	96.3
0. Phosphate (total)	30	1.0	96.7
0. Phosphate (soluble)	26	1.0	96.2
MBAS	4.2	0.15	96.4
Fecal Coliform	5×10^5/100 ml	225/100 ml	99.96
Fecal Strep	6.5×10^5/100 ml	1150/100 ml	99.82
Average Flow (MGD)	-	1.5	-
Average Lime Dose	-	345 mg/l	-
Lead Tower	5 ft of twice-regenerated + 5 ft of virgin carbon		
Polish Tower	8 ft of twice-regenerated + 2 ft of virgin carbon		

*All units in mg/l unless indicated.
The "INFLUENT" is the secondary effluent going to the solids contact clarifier.
The "EFFLUENT" is the final polish carbon tower effluent.
Influent to tertiary plant is from a trickling filter plant with a flow of 23 to 25 MGD; trickling filter plant capacity is 13 MGD.

TABLE 14 "COMPARISON OF WASTEWATER STRENGTH BATTELLE AND CRSD TEST PROGRAMS"

	Probability (% of Occurrences)		
	10	50	90
Battelle Series (1970-71) BOD	180 mg/l	240 mg/l	320 mg/l
CRSD Series (1974-75) BOD	115 mg/l	170 mg/l	250 mg/l
Battelle Series (1970-71) COD	320 mg/l	500 mg/l	720 mg/
CRSD Series (1974-75) COD	215 mg/l	350 mg/l	580 mg
Battelle Series (1970-71) BOD/COD	0.56	0.48	0.44
CRSD Series (1974-75) BOD/COD	0.53	0.48	0.43

TABLE 15 "EFFECT OF POST-OZONATION ON EFFLUENT ORGANIC QUALITY"

CRSD PILOT-PLANT TEST RESULTS*

Parameter	Before Ozonation	After Ozonation
BOD (unfiltered)	32 mg/l	31 mg/l
BOD (filtered)	25 mg/l	24 mg/l
COD (unfiltered)	72 mg/l	66 mg/l
COD (filtered)	59 mg/l	52 mg/l
TOC	31 mg/l	29 mg/l

*All data represent average values over an eleven day period. Ozone dosage ranges from 4 - 9 mg/l.

TABLE 16 "QUALITY OF RAW WASTEWATER"

GARLAND PHYSICAL/CHEMICAL TREATMENT FACILITY

Parameter	Results
Total BOD (mg/l)	266
Filtered BOD (mg/l)	236
Total COD (mg/l)	542
Filtered COD (mg/l)	240
Suspended Solids (mg/l)	233
Alkalinity (mg/l as $CaCO_3$)	200
pH	7.2 - 7.7
PO_4 (mg/l)	15

TABLE 17 "PCT SYSTEM DESIGN DATA" (24)

CHEMICAL TREATMENT SYSTEM

1.	Flocculation: Detention Time, minutes		45
	Chemical Dosage	Alum, mg/l Al	22
		polymer, mg/l	0.25
2.	Sedimentation: Detention Time, hrs.		1.5
	Overflow Rate, gpd/sq ft		900
	Underflow, % of plant flow		1.25
	Underflow solids, % by weight		2
3.	Gravity Thickening: Solids Loading, lb/day-sq ft		12
	Underflow solids, % by weight		4
4.	Vacuum Filtration: Yield, lb/hr-sq ft		2
	Cake solids		18
5.	Sludge Incineration: Solids Loading, lb/hr-sq ft		2

CARBON TREATMENT SYSTEM

1.	Carbon Contacting (8 x 30 mesh carbon) Empty-bed contact time	25
	Hydraulic surface Loading, gpm/sq ft	4
	Backwash volume, % of plant flow	5
	Sodium Nitrate dosage, mg/l N	5.5
	Carbon Dosage, lb/MG	250
	Carbon Regeneration loss, %	5

TABLE 18 "SUMMARY OF PHYSICAL/CHEMICAL TREATMENT SYSTEM PERFORMANCE" (24)

Parameters	Raw Sewage	Clarified Effluent	Carbon Effluent	Average Percent Removal: Chemical Treatment	Average Percent Removal: Carbon Treatment	Average Percent Removal: Overall	AS Effluent*
Suspended Solids (mg/l)	199	28.3	6.7	85.8	76.3	96.6	11.6
Turbidity (JTU)		22.9	6.3		72.5		7.7
TCOD (mg/l)	321	95.8	19.3	70.2	79.9	94.0	39.5
DCOD (mg/l)	49.4	48.6	13.5	1.6	72.2	72.7	25.7
BOD (mg/l)		36.2	7.8		78.5		8.0
Total Phosphate (mg/l P)	11.1	1.3	0.9	88.3	30.8	91.9	
Nitrate (mg/l N)		0.9	1.3				
Color		20	7.8		61.0		33.1
pH	7.7	6.8	6.8				

Notes: 1. Average alum dosage = 25 mg/l Al (275 mg/l alum)
2. Average polymer dosage = 0.3 mg/l Calgon WT-3,000
3. AS Effluent refers to Activated Sludge Plant Effluent (8 MGD, existing facility)

TABLE 19 "EFFECT OF REGENERATION ON THE PCT CARBON CHARACTERISTICS"

Carbon Characteristics	Virgin Carbon	Spent Carbon (Composite Sample) 1st Reg.	2nd Reg.	3rd Reg.	Regenerated Carbon (Composite Sample) Before Quenching 1st Reg.	2nd Reg.	3rd Reg.	After Quenching 1st Reg.	2nd Reg.	3rd Reg.
Iodine No. (mg/l)	1,040	402	572	570	805	722	773	751	727	721
Apparent Density (g/cm cu ft)	0.484	0.629	0.585	0.594	0.528	0.537	0.526	0.565	0.548	0.535
Molasses No.	222	120	168	154	213	233	230	189	221	204
Methylene Blue No. (mg/g)	259	147	153	153	223	243	246	227	239	245
Ash (%)	6.4	10.3	8.22	8.67	10.7	11.6	7.81	12.0	12.2	9.0
Mean Particle Dia. (mm)	1.44	1.46	1.58	1.48	1.57	1.50	1.54	1.55	1.50	1.43

TABLE 2c.

TERTIARY TREATMENT PLANTS

Site	Status 1973	Design Engineer	Average Plant Capacity (MDG)	Contactor Type	No. of Contactors In Series	Contact Time[1] (Min.)	Hydraulic Loading (gpm/ft^2)	Total Carbon Depth (ft)	Carbon Size	Effluent Requirements[2] (Oxygen Demand)
Arlington, Virginia	Design	Alexander Potter/ Engineering-Science	30	Downflow Gravity	1	38	2.9	15	8 x 30	BOD < 3 mg/l
Colorado Springs, Colo.	Operating Dec.'70 to Present	Arthur B. Chafet & Assoc.	3	Downflow	2	30	5	20	8 x 30	BOD < 2 mg/l
Dallas, Texas	Design	URS Forest & Cotton	100	Upflow Packed	1	10	8	10	8 x 30	BOD < 10 mg/l BOD < 5 mg/l (by 1980)
Fairfax County, Va.	Design	Alexander Potter/ Engineering-Science	36	Downflow Gravity	1	36	3	15	8 x 30	BOD < 3 mg/l
Los Angeles, Calif.	Design	City of Los Angeles	5[3]	Downflow Gravity	2	50	4	26	8 x 30	COD < 12 mg/l
Montgomery County, Md.	Design	CH_2M/Hill	60	Upflow Packed	1	30	6.5	26	8 x 30	BOD < 1 mg/l COD < 10 mg/l
Occoquan, Va.	Design	CH_2M/Hill	18	Upflow Packed	1	30	5.8	24	8 x 30	BOD < 1 mg/l COD < 10 mg/l
Orange County, Calif.	Construction	Orange County Water District	15	Upflow Packed	1	30	5.8	24	8 x 30	COD < 30 mg/l
Piscataway, Md.	Operating Mar.'73 to Present	Roy F. Weston	5	Downflow Pressure	2	37	6.5	32	8 x 30	BOD < 5 mg/l
St. Charles, Missouri	Construction	Moran and Cooke	5.5	Downflow Gravity	1	30	3.7	15	8 x 30	
South Lake Taho, Calif.	Operating Mar.'68 to Present	CH_2M/Hill	7.5	Upflow Packed	1	17	6.2	14	8 x 30	BOD < 5 mg/l COD < 30 mg/l
Windhoek, South Africa	Operating Oct.'68 to Present	National Institute for Water Research Pretoria, So. Africa	1.3	Downflow Pressure	2	30	3.8	15	12 x 40	COD < 10 mg/l

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[1] Empty bed (superficial) contact time for average plant flow.

[2] BOD: Biochemical oxygen demand
COD: Chemical oxygen demand

[3] 50 MGD ultimate capacity

TABLE 21

PHYSICAL/CHEMICAL TREATMENT PLANTS

Site	Status 1973	Design Engineer	Average Plant Capacity (MGD)	Contact Time[1] (Min.)	Hydraulic Loading (gpm/ft^2)	Total Carbon Depth (ft)	Carbon Size	Effluent Requirements[2] (oxygen Demand)
Cortland, New York	Design	Stearns & Wheeler	10	30	4.3	17	8 x 30	TOD 30 mg/1
Cleveland Westerly, Ohio	Construction	Engineering-Science	50	30	3.7	17	8 x 30	BOD 20 mg/1
Fitchburg, Massachusetts	Construction 95% Complete	Camp Dresser & McKee	15	35	3.3	15.5	8 x 30	BOD 10 mg/1
Garland, Texas	Construction	URS Forest & Cotton	30	30	2.5	10	8 x 30	BOD 10 mg/1
LeRoy, New York	Design	Lozier Engineers	1	27	7.3	26.8	12 x 40	BOD 10 mg/1
Niagara Falls, New York	Construction 50% Complete	Camp Dresser & McKee	48	20	3.3	9	8 x 30	COD 112 mg/1
Owosso, Michigan	Design	Ayres, Lewis, Norris & May	6	36	6.2	30	12 x 40	BOD 10 mg/1
Rosemount, Minnesota	Operational	Banister, Short, Elliot, Hendrickson and Associates	0.6	66 (max)	4.2	36 (max)	12 x 40	BOD 10 mg/1
Rocky River, Ohio	Operational	Willard Schade & Assoc.	10	26	4.3	15	8 x 30	BOD 15 mg/1
Vallejo, California	Design	Kaiser Engineers	13	26	4.6	16	12 x 40	BOD 45 mg/1 (90% of time)

[1] Empty bed (superficial) contact time for average plant flow.

[2] BOD: Biochemical oxygen demand
COD: Chemical oxygen demand

TABLE 22 "SUMMARY OF PCT PILOT-PLANT AND FULL-SCALE PLANT PERFORMANCES"

	Effluent			Effluent			Effluent		
	Raw COD (mg/l)	COD (mg/l)	% Removal	Raw TOC (mg/l)	TOC (mg/l)	% Removal	Raw BOD (mg/l)	BOD (mg/l)	% Removal
Blue Plains Pilot Plant	320	16	95	100	8	92	150	6	96
Owosso, Michigan	250-350	24-30	-91	-	-	-	140	8	84
Pomona, California	321	19	94	-	-	-	120[1]	7.8	78.5[2]
Rosemount, Minnesota (1st year)	-	-	-	-	-	-	230	23	90
Rosemount, Minnesota (last 3 to 4 months)									
Battelle Pilot Plant at Westerly	527	42	92	-	-	-	240	26	89
CRSD Pilot Plant at Westerly	437	56	87	90	21	77	206	32	84

[1] Estimated based on BOD similar to COD removals across clarifier.

[2] Just around carbon columns.

TABLE 23 "CARBON PILOT-PLANT RESULTS FOR PETROCHEMICAL AND REFINING WASTEWATERS"

Type of Wastewater	Design Q (MGD)	Process Application	Influent COD (mg/l)	Effluent COD (mg/l)	Percent Removal
Refinery	28	Physical/Chemical	600	103	83
Refinery	1.9	Physical/Chemical	800	201	75
Refinery	22	Physical/Chemical	670	143	79
Petrochemical	3	Tertiary	150	49	67
Refinery	26	Tertiary	100	41	59
Refinery	28	Tertiary	300	50	83
Refinery	8	Tertiary	100	40	60
Petrochemical	29	Tertiary	150	48	68

TABLE 24 "REFINERY WASTEWATER TREATMENT RESULTS"

Parameter	API Separator Effluent	Carbon Treated Effluent	Biologically Treated Effluent	Biological-Carbon Treated Effluent
BOD (mg/l)	97	48	7	3
COD (mg/l)	234	103	98	26
TOC (mg/l)	56	14	30	7
Oil & Grease (mg/l)	29	10	10	7
Phenols (mg/l)	3.4	0.004	0.01	0.001
Chromium (mg/l)	2.2	0.2	0.9	0.02
Copper (mg/l)	0.5	0.03	0.1	0.05
Iron (mg/l)	2.2	0.3	3	0.9
Lead (mg/l)	0.2	0.2	0.2	0.2
Zinc (mg/l)	0.7	0.08	0.4	0.15
Sulfide (mg/l)	33	39	0.2	0.2
Ammonia (mg/l)	28	28	27	27
Cyanides (mg/l)	0.25	0.2	0.2	0.2
Turbidity, (TTU)	26	11	17	5
Color (Std. Color Units)	30	15	15	1

TABLE 25 "CARBON REGENERATION ACTIVITY ANALYSIS"

	Iodine No.	Molasses No.
Virgin Carbon	1,010	216
API Separator Effluent to Carbon	906	405
Biologically Treated Effluent to Carbon	991	304

TABLE 26 "PILOT-PLANT RESULTS-TERTIARY CARBON APPLICATION"

	Influent Concentration	Effluent Concentration		Average Percentage Removal	
COD (mg/l)	600	280[1]		53[1]	
	500	230		54	
	400	175		56	
	300	120		60	
	200	65		68	
SOC (mg/l)	300	140[2]	250[3]	53[2]	17[3]
	200	95	155	53	23
	100	30	55	70	45
	50	10	25	80	50
BOD (mg/l)	250	88[4]	218[5]	65[4]	13[5]
	200	70	186	65	7
	150	54	135	64	10
	100	36	68	64	32
	50	20	30	60	40
	20	10	12	50	40

[1] Throughput Rate = 0.6 - 1.2 Bed Volumes per hour
[3] Throughput Rate = 2.4 Bed Volumes per hour
[5] Throughput Rate = 1.2 Bed Volumes per hour
[2] Throughput Rate = 0.5 Bed Volumes per hour
[4] Throughput Rate = 0.15 Bed Volumes per hour

TABLE 27 "DESIGN CRITERIA FOR THE ARCO CARBON PLANT"

Number of Rainfall Days Per Year (max.)	30	days
Maximum Rainfall Runoff Rate (per day)	12.6	Million Gallons
Maximum Rainfall Runoff Rate (per year)	378	Million Gallons
Average Influent COD Concentration	250	mg/l
Average Effluent COD Concentration	37	mg/l
Carbon Capacity	1	lb carbon exhausted per 1000 gal. water treated (1.75 lb COD removed/lb carbon)

TABLE 28 "ACTIVATED CARBON ADSORPTION DESIGN DATA AND ACTIVATED CARBON PROPERTIES"

Rated Flow (Each of Three Adsorbers)		667	gpm
Adsorber Diameter		10	ft
Adsorber Bed Depth		45	ft
Contact Time (Empty Bed)		40	min
Hydraulic Loading		8.5	gpm/ft^2
Design Inlet Pressure		60	psi
Pressure Drop Through Carbon		35	psi
Carbon Inventory	Carbon Bed	92,000	lb
	Adsorber Total	100,000	lb
Theoretical Carbon Capacity		0.3	lb TOC/lb carbon
Carbon Dosage		0.86 lb carbon/1,000 gal Throughput	

Activated Carbon Properties Filtrasorb 300
(8 x 30 Bituminous Coal)

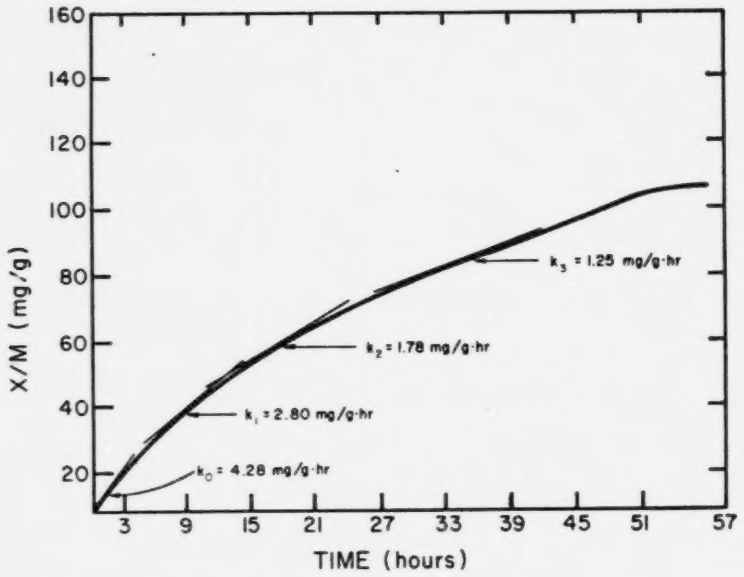
Total Surface Area (N_2 BET Method)	950-1050	m^2/g
Bulk Density	26	lb/ft^3
Particle Density Wetted in Water	1.3-1.4	g/cc
Mean Particle Diameter	1.5-1.7	mm
Iodine Number, minimum	950	
Ash	Max 8%	
Moisture	Max 2%	

TABLE 29 "THERMAL REGENERATION DESIGN DATA"

Furnace		60" x 6 Hearth with Integral Afterburner
Regeneration Rate		125 lb/hr
Steam Addition Rate		125 lb/hr
Fuel		Refinery Fuel Gas
Fuel Rate	Hearth 4	188 CFH
	Hearth 6	68 CFH
	Afterburner	310 CFH
Combustion Air Rate	Hearth 4	5,000 CFH
	Hearth 6	1,800 CFH
	Afterburner	8,120 CFH
Design Temperatures	Hearth 4	1,725° F
	Hearth 6	1,750° F
	Afterburner	1,250° F

FIGURE 1

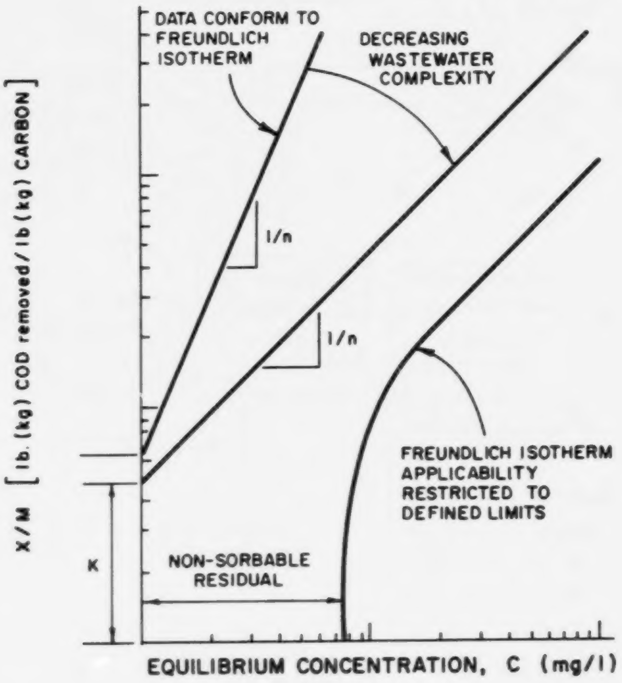
ADSORPTION OF DBS TO EQUILIBRIUM IN CONTINUOUSLY STIRRED FLOW SYSTEMS[2]



ORGANIC CONSTITUENT IS DODECYL-BENZENESULFONATE (DBS)

Figure 2

FREUDLICH ISOTHERM APPLICATION [3]


DATA CONFORM TO FREUNDLICH ISOTHERM
DECREASING WASTEWATER COMPLEXITY
1/n
1/n
FREUNDLICH ISOTHERM APPLICABILITY RESTRICTED TO DEFINED LIMITS
X/M [lb. (kg) COD removed/lb (kg) CARBON]
K
NON-SORBABLE RESIDUAL
EQUILIBRIUM CONCENTRATION, C (mg/l)

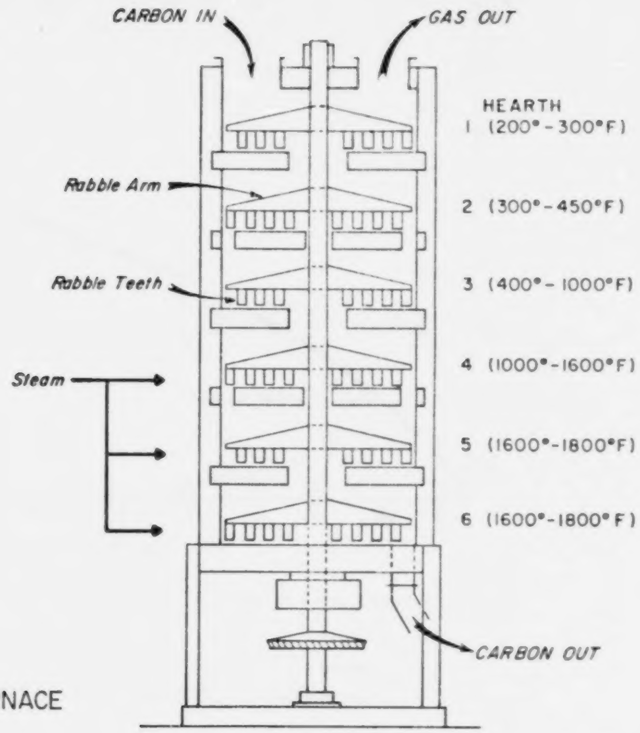

CARBON IN
GAS OUT
HEARTH
1 (200°-300°F)
Rabble Arm
2 (300°-450°F)
Rabble Teeth
3 (400°-1000°F)
Steam
4 (1000°-1600°F)
5 (1600°-1800°F)
6 (1600°-1800°F)
CARBON OUT

FIGURE 3

CROSS-SECTIONAL VIEW
OF MULTIPLE-HEARTH FURNACE

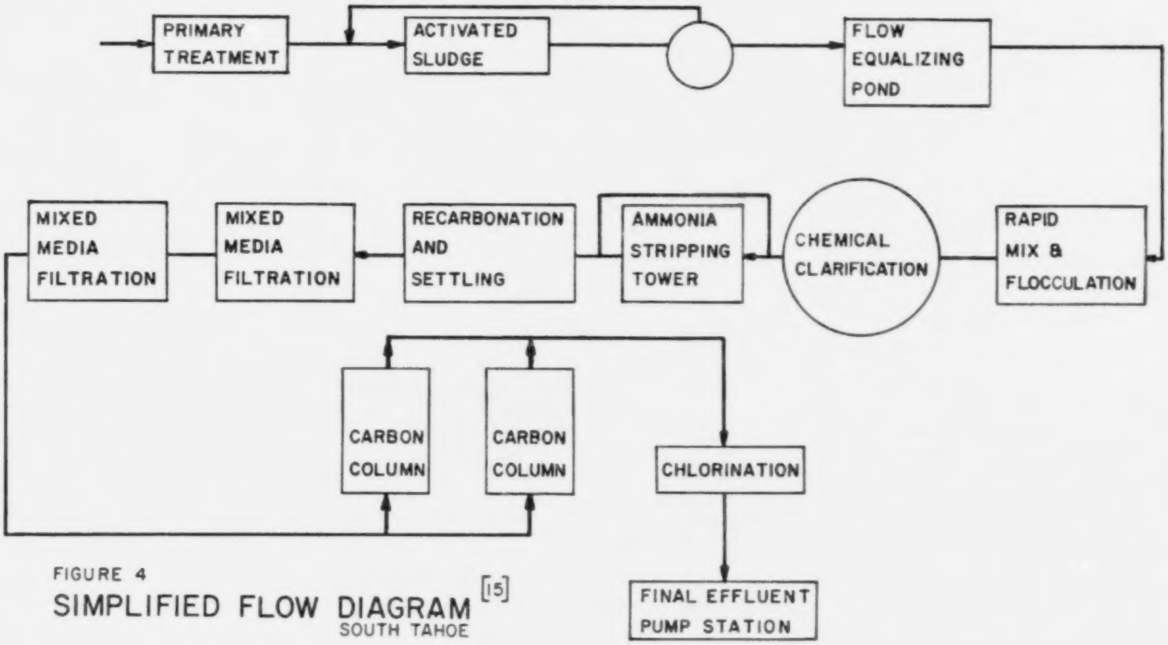

PRIMARY TREATMENT
ACTIVATED SLUDGE
FLOW EQUALIZING POND
RAPID MIX & FLOCCULATION
CHEMICAL CLARIFICATION
AMMONIA STRIPPING TOWER
RECARBONATION AND SETTLING
MIXED MEDIA FILTRATION
MIXED MEDIA FILTRATION
CARBON COLUMN
CARBON COLUMN
CHLORINATION
FINAL EFFLUENT PUMP STATION

FIGURE 4

SIMPLIFIED FLOW DIAGRAM [15]
SOUTH TAHOE

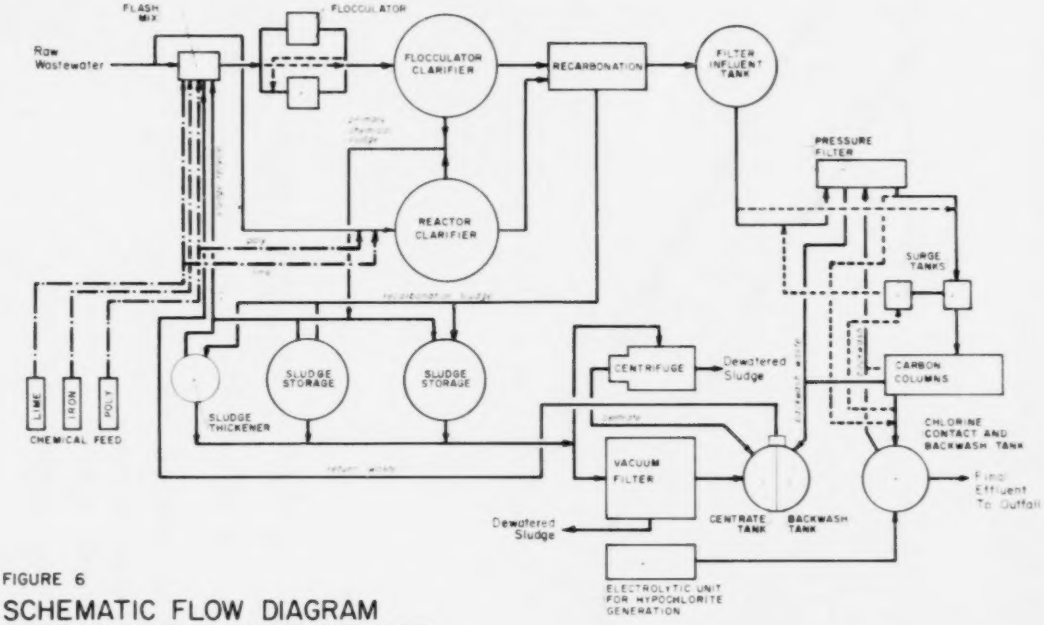

FLASH MIX
FLOCCULATOR
Raw Wastewater
FLOCCULATOR CLARIFIER
RECARBONATION
FILTER INFLUENT TANK
primary chemical sludge
REACTOR CLARIFIER
poly
lime
recarbonation sludge
PRESSURE FILTER
SURGE TANKS
LIME
IRON
POLY
CHEMICAL FEED
SLUDGE THICKENER
SLUDGE STORAGE
SLUDGE STORAGE
CENTRIFUGE
Dewatered Sludge
CARBON COLUMNS
centrate
return water
VACUUM FILTER
CENTRATE TANK
BACKWASH TANK
CHLORINE CONTACT AND BACKWASH TANK
Final Effluent To Outfall
Dewatered Sludge
ELECTROLYTIC UNIT FOR HYPOCHLORITE GENERATION

FIGURE 6

SCHEMATIC FLOW DIAGRAM
WESTERLY ADVANCED WASTE TREATMENT PLANT
PILOT PLANT

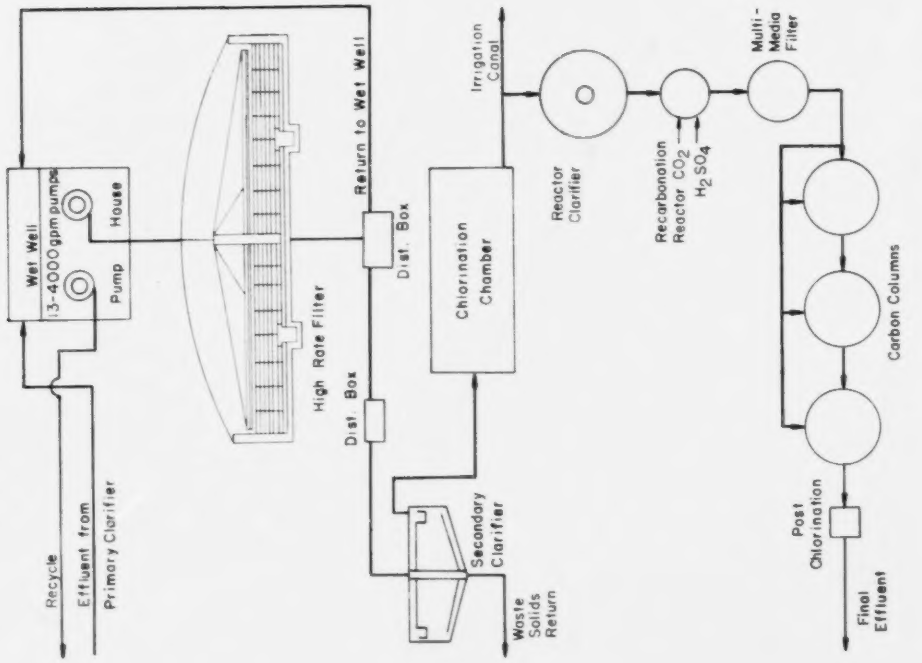

Recycle
Effluent from Primary Clarifier
Wet Well
13-4000 gpm pumps
Pump House
High Rate Filter
Return to Wet Well
Dist. Box
Dist. Box
Secondary Clarifier
Waste Solids Return
Chlorination Chamber
Irrigation Canal
Reactor Clarifier
Recarbonation Reactor
CO_2
H_2SO_4
Multi-Media Filter
Carbon Columns
Post Chlorination
Final Effluent

FIGURE 5
SIMPLIFIED FLOW DIAGRAM
COLORADO SPRINGS PLANT

FIGURE 7

FREQUENCY ANALYSIS FOR EFFLUENT BOD[25]

CRSD PRECARBON OZONATION STUDY
WESTERLY PILOT PLANT

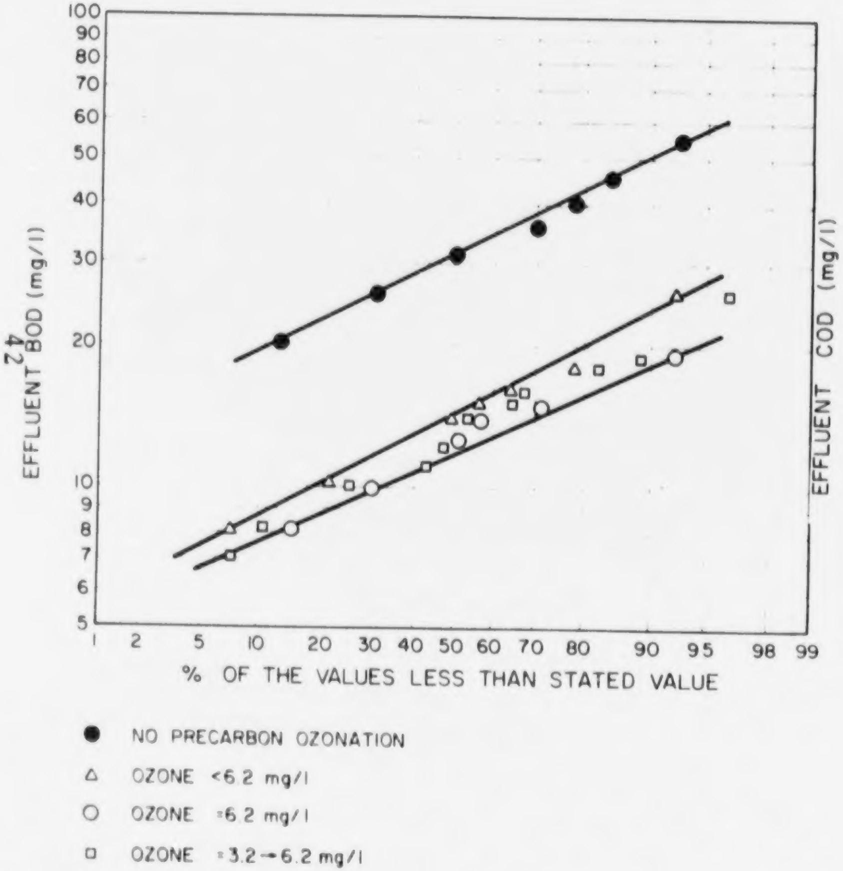


FIGURE 8

FREQUENCY ANALYSIS FOR EFFLUENT COD[25]

CRSD PRECARBON OZONATION STUDY
WESTERLY PILOT PLANT

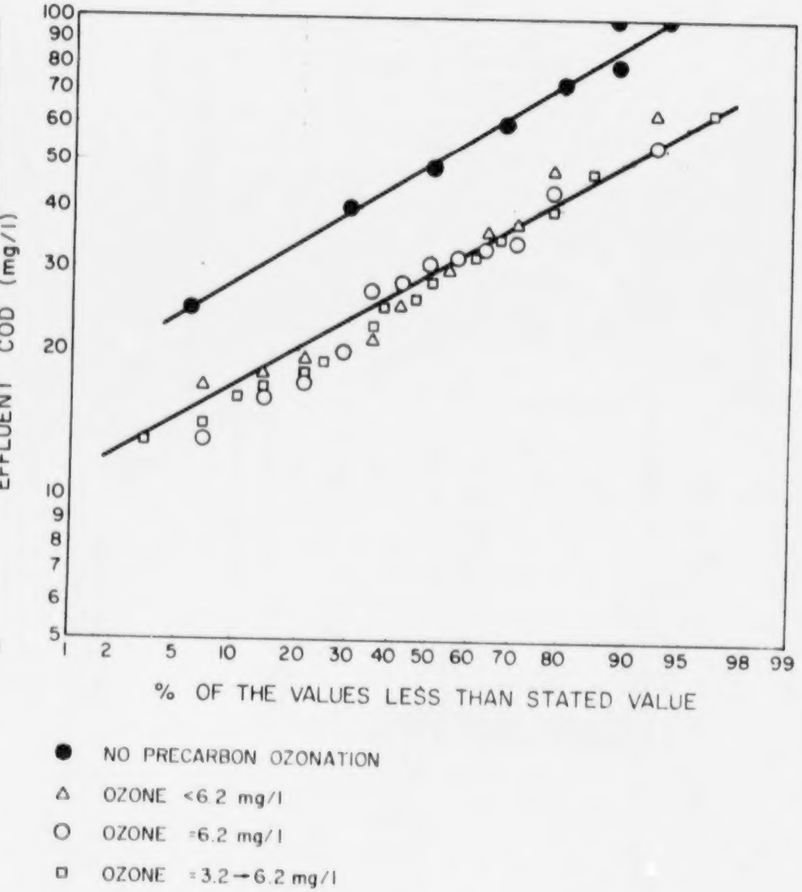


FIGURE 9

FLOW DIAGRAM FOR THE GARLAND PLANT [22]

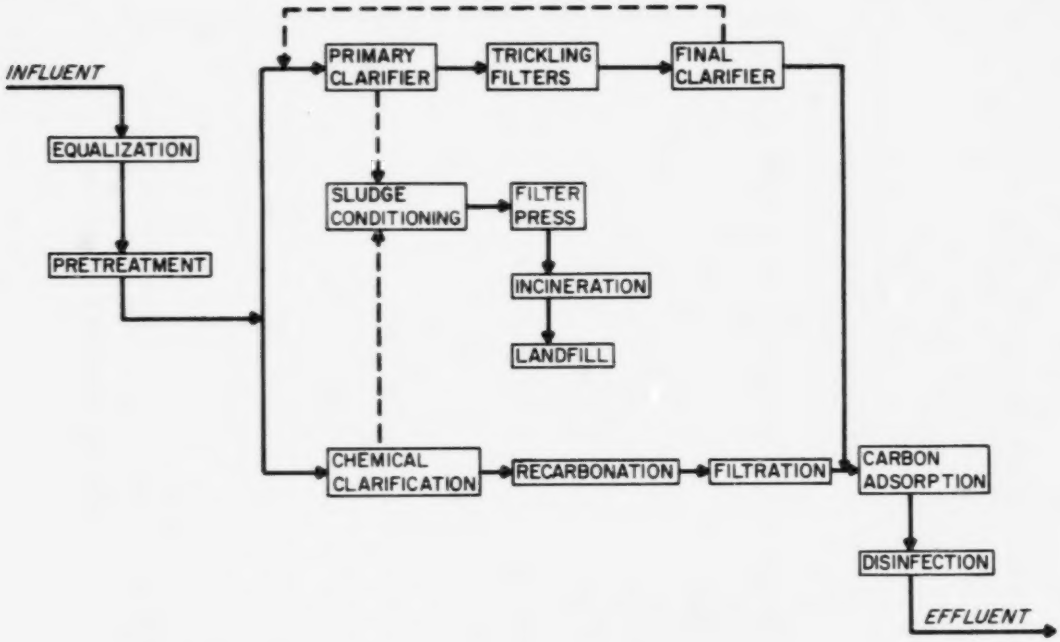

INFLUENT
EQUALIZATION
PRETREATMENT
PRIMARY CLARIFIER
TRICKLING FILTERS
FINAL CLARIFIER
SLUDGE CONDITIONING
FILTER PRESS
INCINERATION
LANDFILL
CHEMICAL CLARIFICATION
RECARBONATION
FILTRATION
CARBON ADSORPTION
DISINFECTION
EFFLUENT

FIGURE 10

PHYSICAL/CHEMICAL PILOT PLANT SCHEMATIC

POMONA, CALIFORNIA

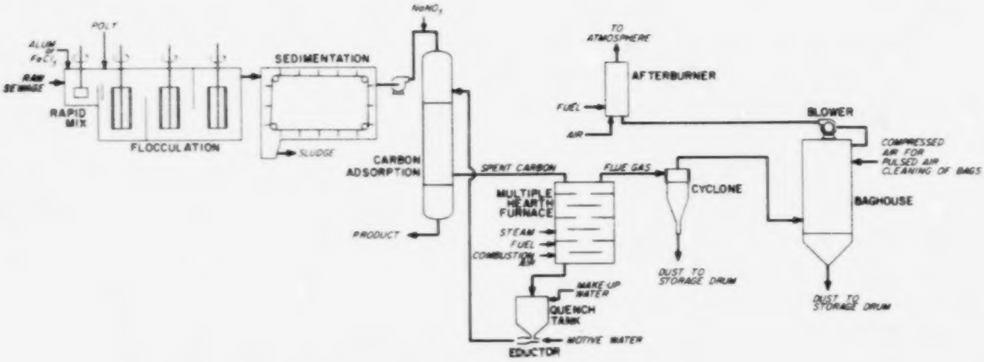

ALUM or $FeCl_3$
POLY
RAW SEWAGE
RAPID MIX
FLOCCULATION
SEDIMENTATION
SLUDGE
$NaNO_3$
CARBON ADSORPTION
PRODUCT
SPENT CARBON
MULTIPLE HEARTH FURNACE
STEAM
FUEL
COMBUSTION AIR
MAKE-UP WATER
QUENCH TANK
MOTIVE WATER
EDUCTOR
TO ATMOSPHERE
AFTERBURNER
FUEL
AIR
FLUE GAS
CYCLONE
DUST TO STORAGE DRUM
BLOWER
COMPRESSED AIR FOR PULSED AIR CLEANING OF BAGS
BAGHOUSE
DUST TO STORAGE DRUM

FIGURE 11

SULFIDES AND HEADLOSS vs TIME

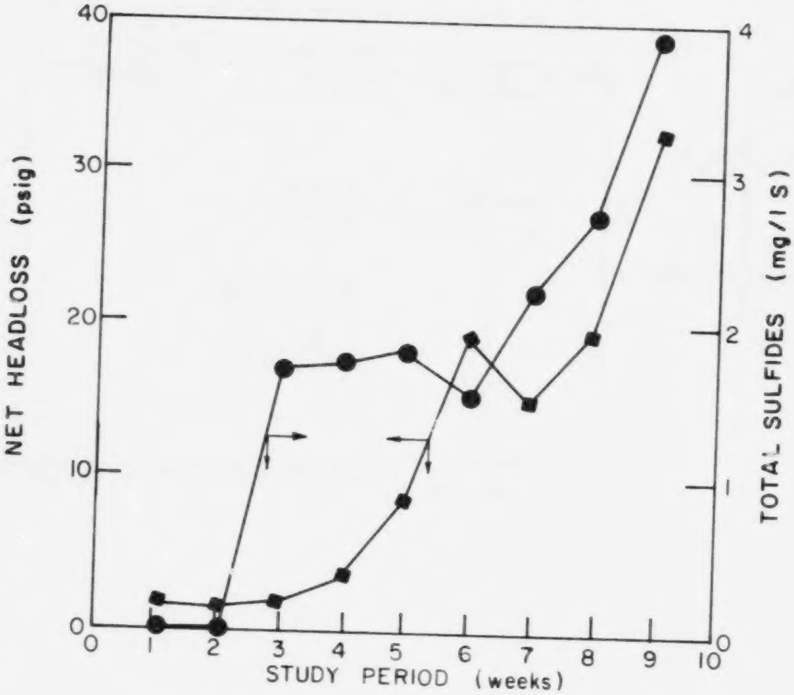


FIGURE 12

BOD REMOVAL TREATMENT RESULTS[27]

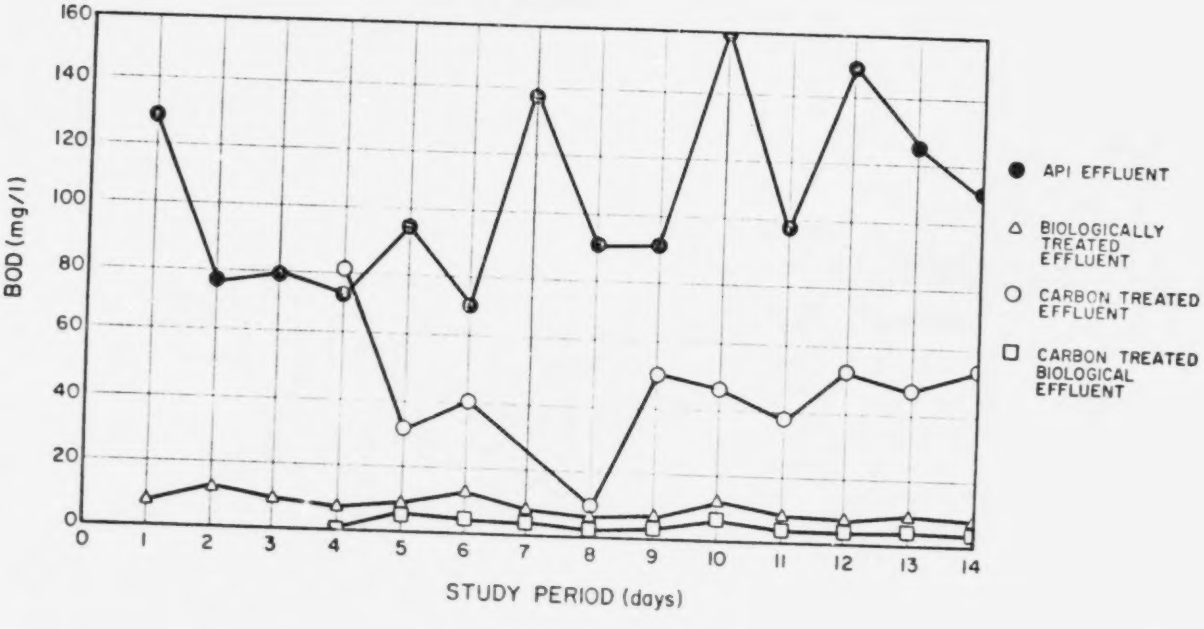


FIGURE 13

COD REMOVAL TREATMENT RESULTS [27]

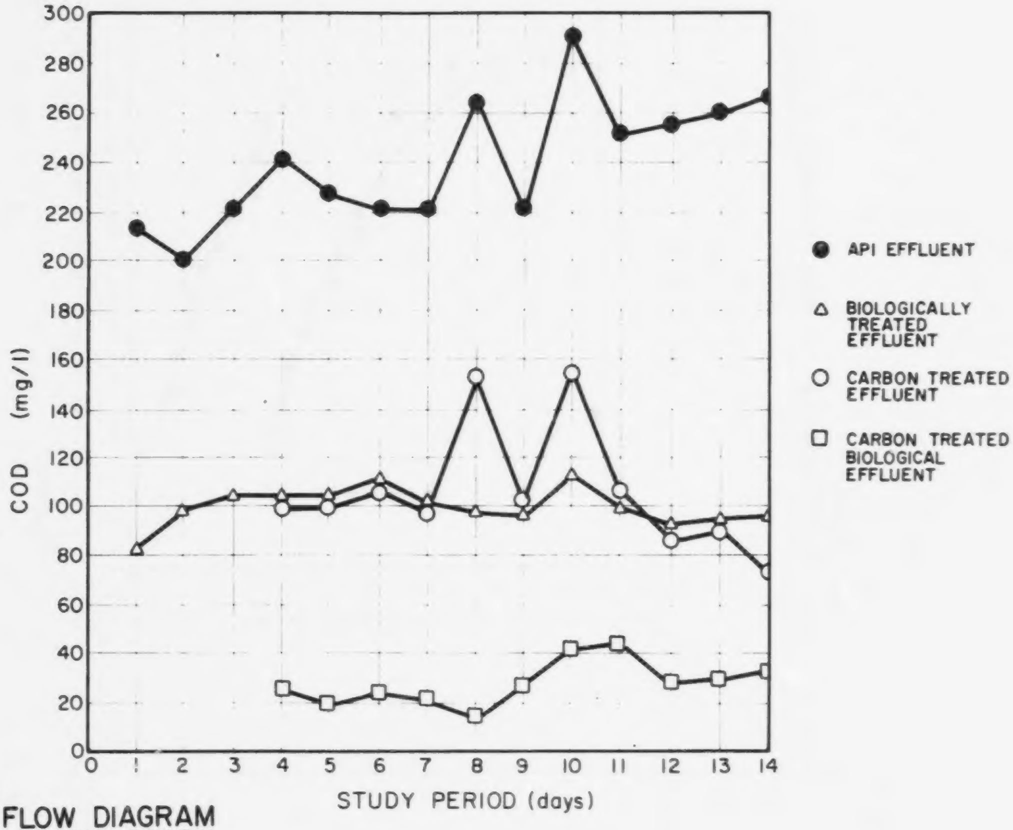
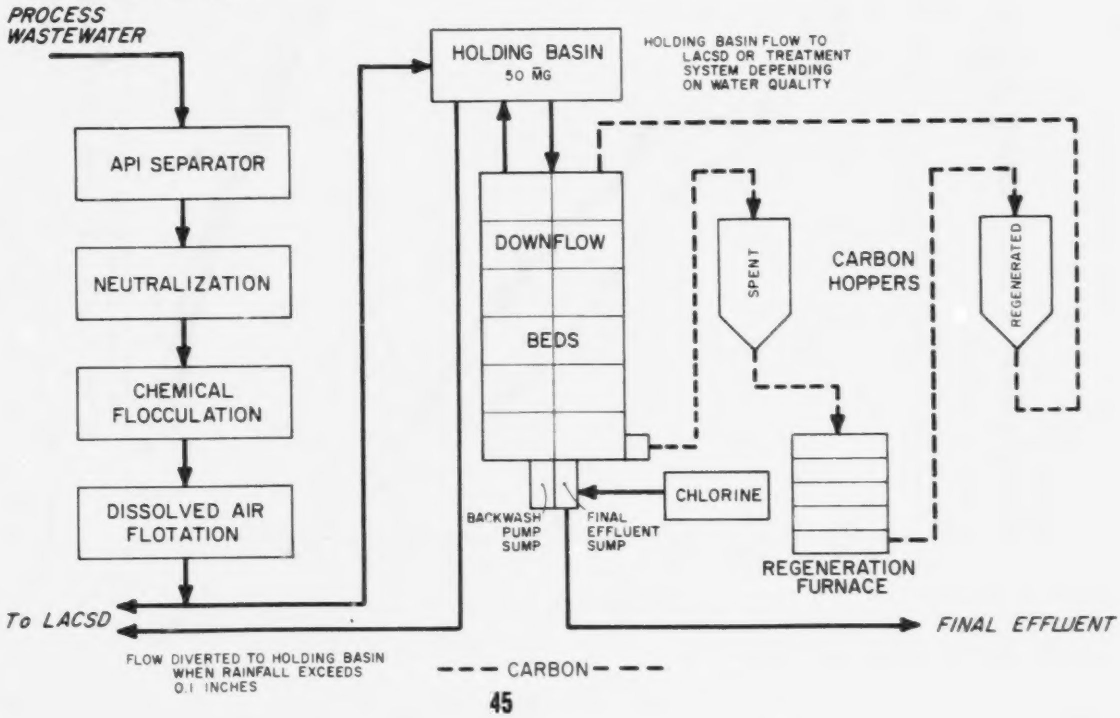


FIGURE 14

ARCO FLOW DIAGRAM

WATSON REFINERY



PROCESS WASTEWATER
API SEPARATOR
NEUTRALIZATION
CHEMICAL FLOCCULATION
DISSOLVED AIR FLOTATION
To LACSD
FLOW DIVERTED TO HOLDING BASIN WHEN RAINFALL EXCEEDS 0.1 INCHES
HOLDING BASIN
50 MG
HOLDING BASIN FLOW TO LACSD OR TREATMENT SYSTEM DEPENDING ON WATER QUALITY
DOWNFLOW
BEDS
BACKWASH PUMP SUMP
FINAL EFFLUENT SUMP
CHLORINE
SPENT
CARBON HOPPERS
REGENERATED
REGENERATION FURNACE
FINAL EFFLUENT
CARBON

FIGURE 15

PERFORMANCE OF ARCO CARBON PLANT
COD REMOVAL

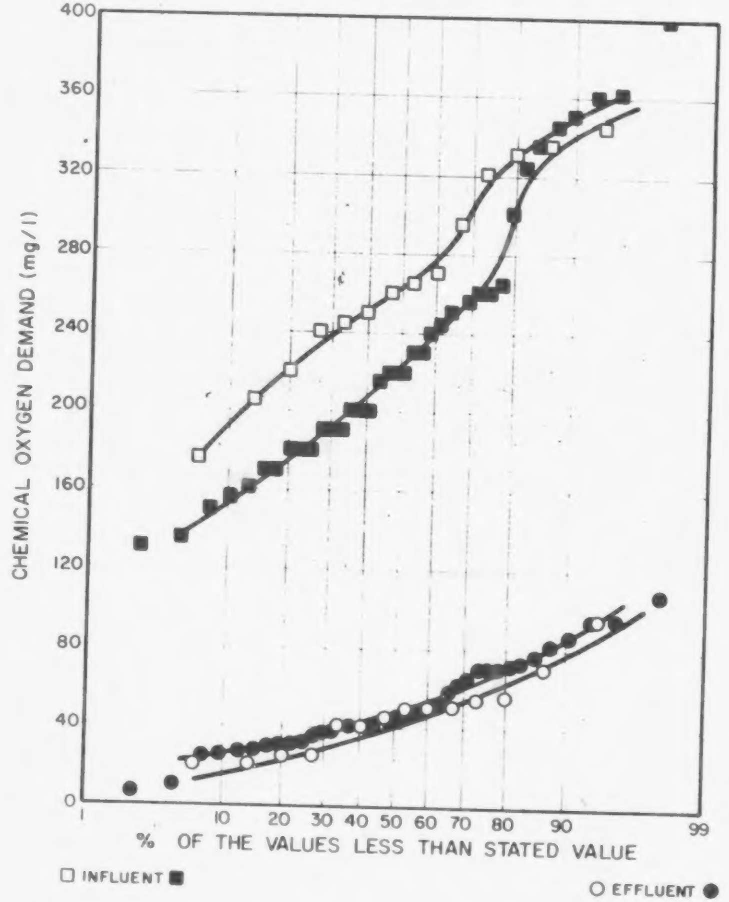


FIGURE 16

PERFORMANCE OF ARCO CARBON PLANT
O&G REMOVAL

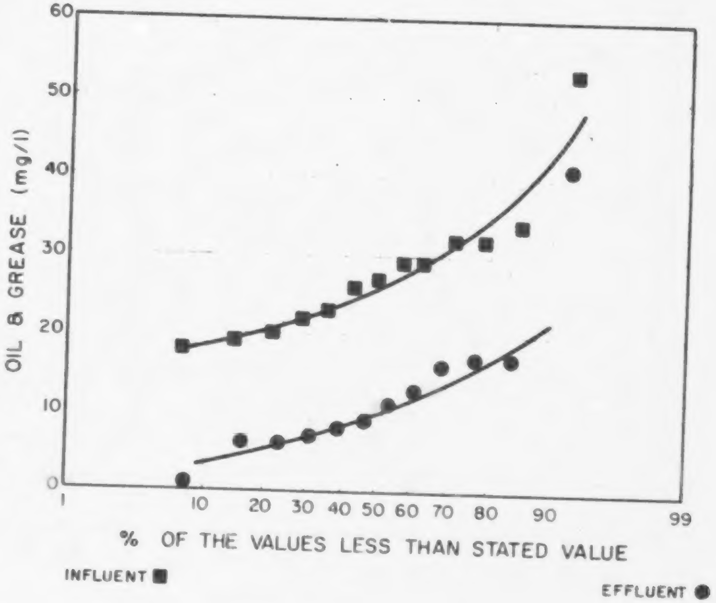


FIGURE 17

CARBON TREATMENT SYSTEM

REICHHOLD CHEMICALS CO.

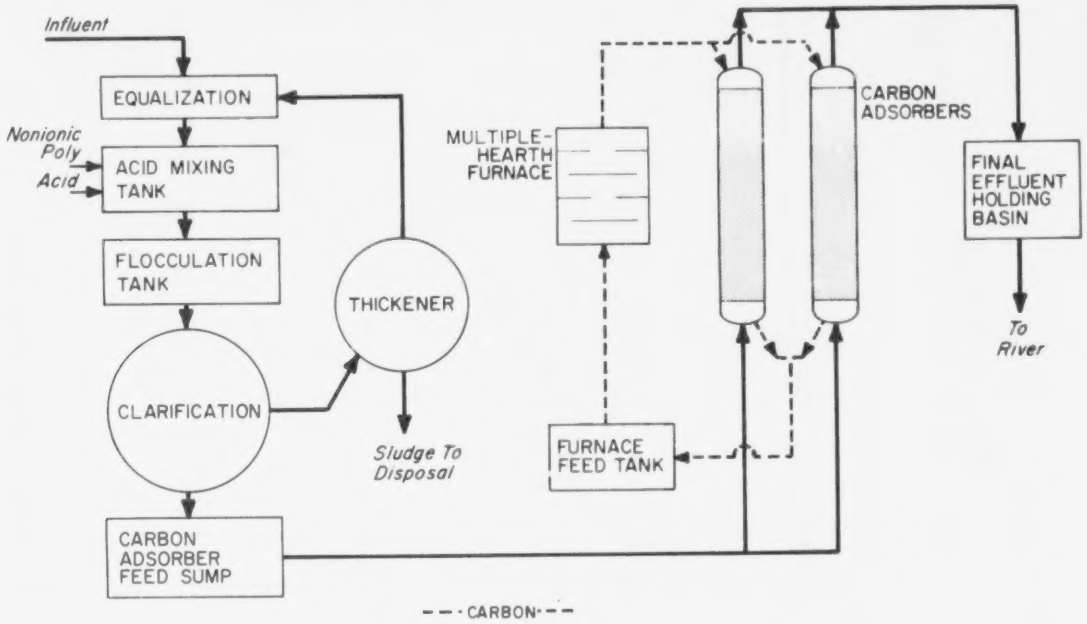

Influent
EQUALIZATION
Nonionic Poly
Acid
ACID MIXING TANK
FLOCCULATION TANK
THICKENER
CLARIFICATION
Sludge To Disposal
CARBON ADSORBER FEED SUMP
MULTIPLE-HEARTH FURNACE
FURNACE FEED TANK
CARBON ADSORBERS
FINAL EFFLUENT HOLDING BASIN
To River
--- CARBON ---

FIGURE 18

BP TREATMENT SYSTEM FLOW DIAGRAM

MARCUS HOOK REFINERY

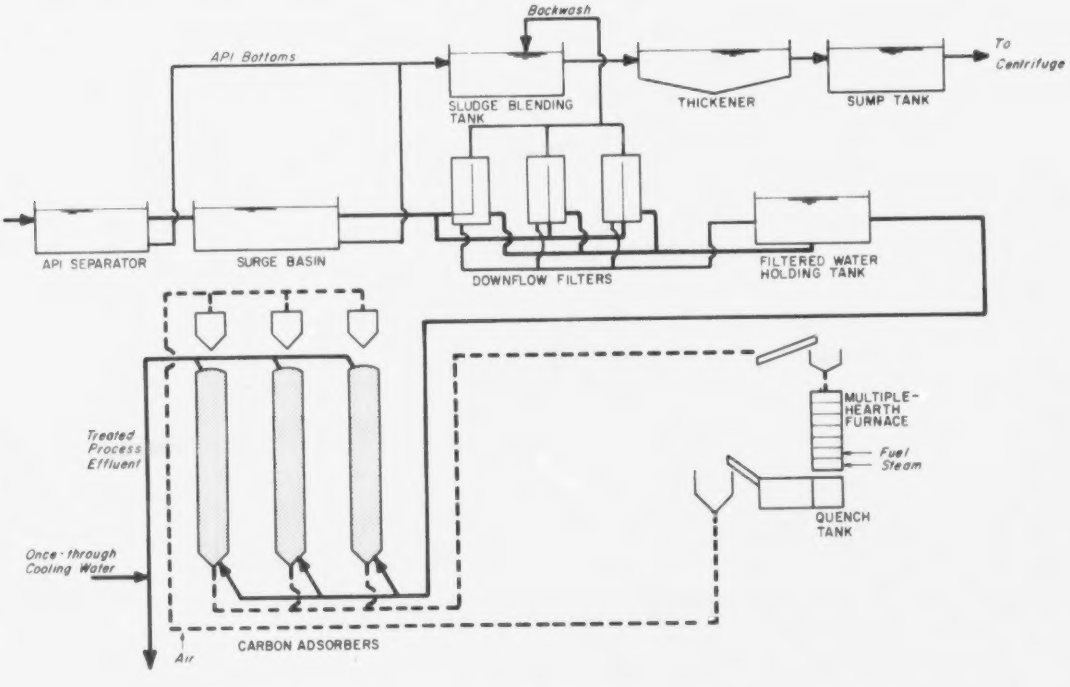

Backwash
API Bottoms
SLUDGE BLENDING TANK
THICKENER
SUMP TANK
To Centrifuge
API SEPARATOR
SURGE BASIN
DOWNFLOW FILTERS
FILTERED WATER HOLDING TANK
Treated Process Effluent
Once-through Cooling Water
MULTIPLE-HEARTH FURNACE
Fuel
Steam
QUENCH TANK
Air
CARBON ADSORBERS

FIGURE 19

COD REMOVAL AS A FUNCTION OF ADSORBER CONTACT TIME[32]
PERIOD I

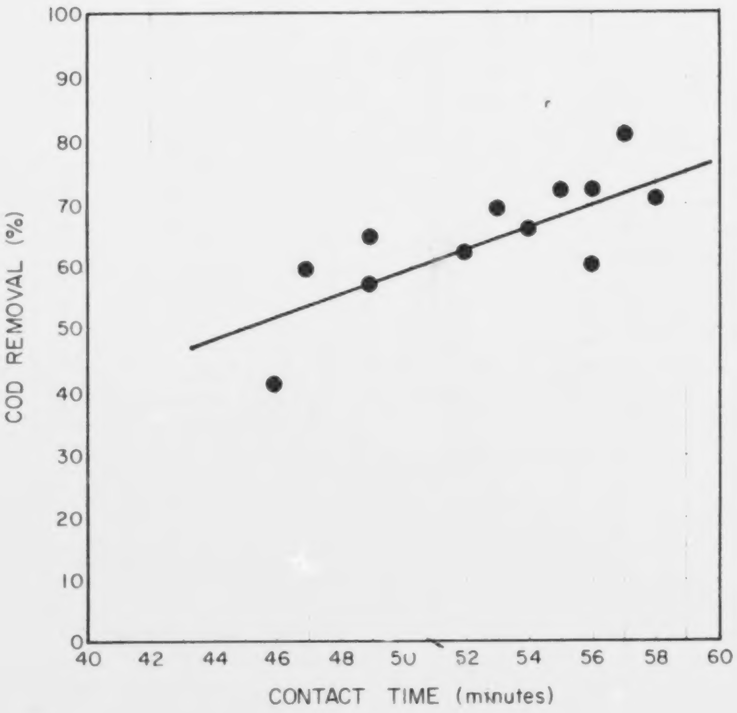


FIGURE 20

ADSORBER OIL REMOVAL AS A FUNCTION OF INFLUENT CONCENTRATION[32]
PERIOD I

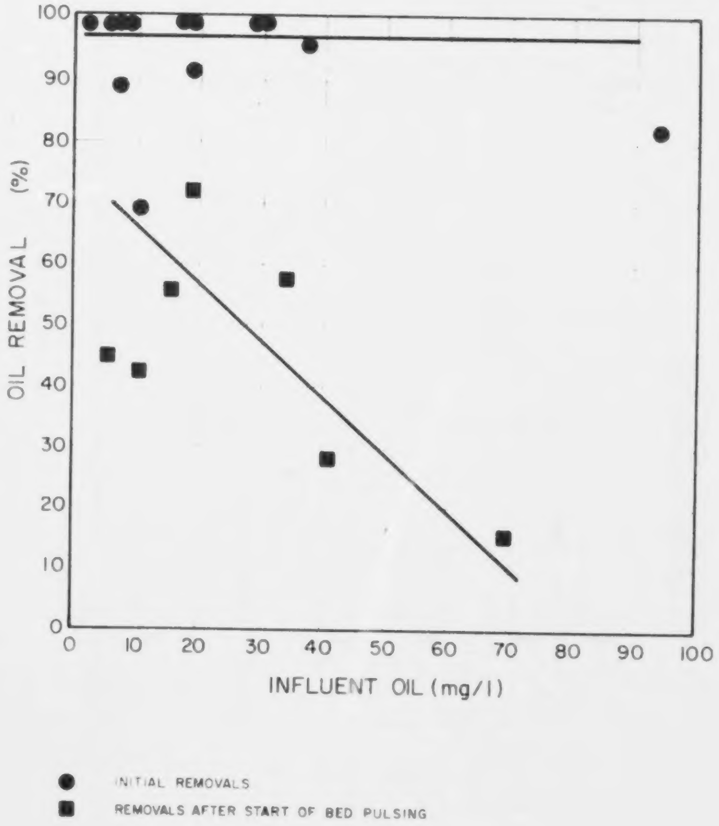
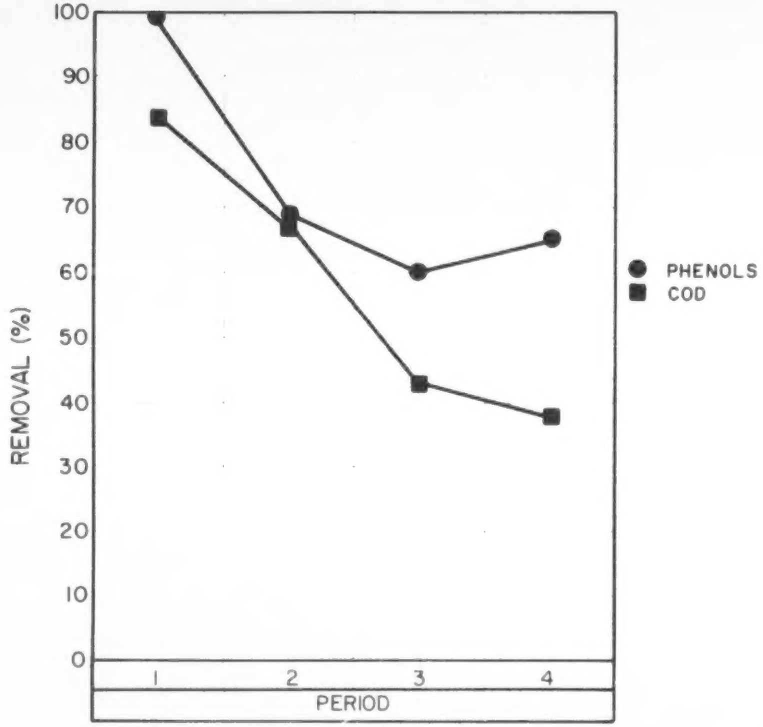


FIGURE 21

FULL-SCALE PROCESS PERFORMANCE
BP MARCUS HOOK



PERIOD
1 VIRGIN CARBON, NO FCCU FOUL CONDENSATE
2 CARBON BEDS NOT TURNED OVER, FCCU CONDENSATE INCLUDED
3 CARBON BEDS TURNED OVER, FCCU CONDENSATE INCLUDED
4 EFFLUENT SEPTUMS BENT, NO FCCU CONDENSATE, ONE YEAR OPERATING

FIGURE 22

EFFLUENT COD ATTAINABLE FROM ACTIVATED CARBON SYSTEMS

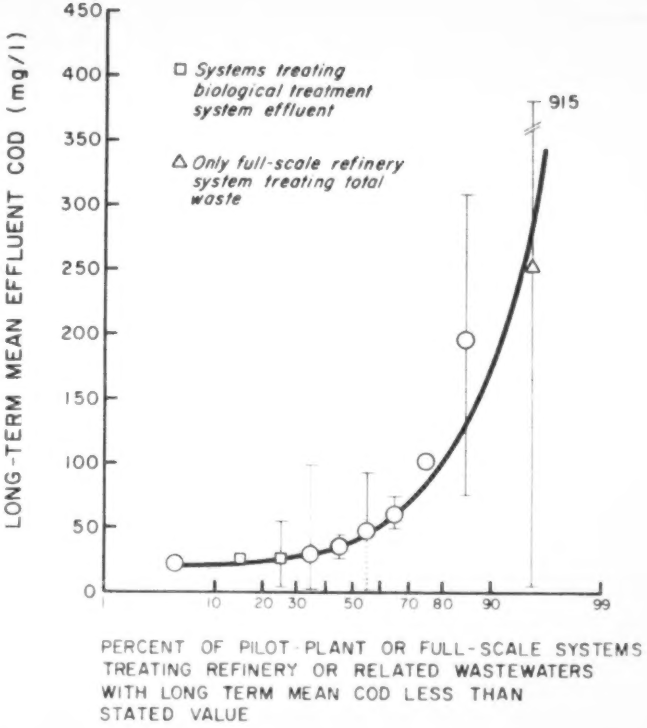


FIGURE 23

INFLUENT AND EFFLUENT OIL AND GREASE DISTRIBUTIONS FOR A FULL-SCALE ACTIVATED CARBON SYSTEM

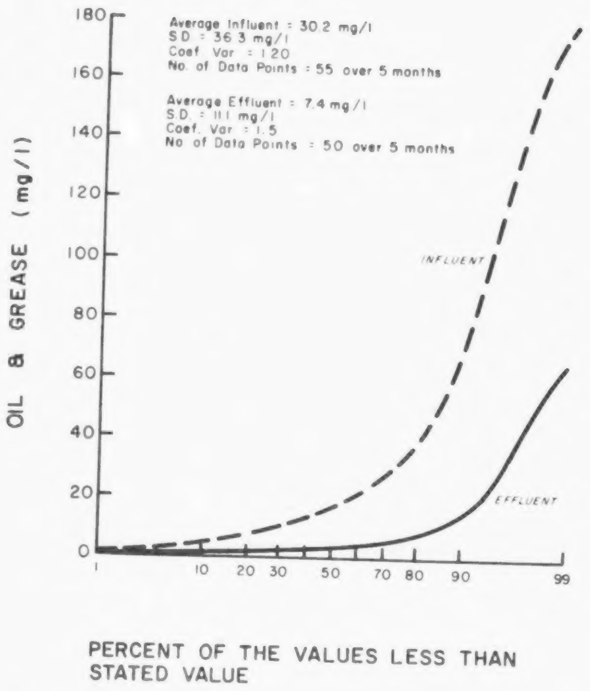
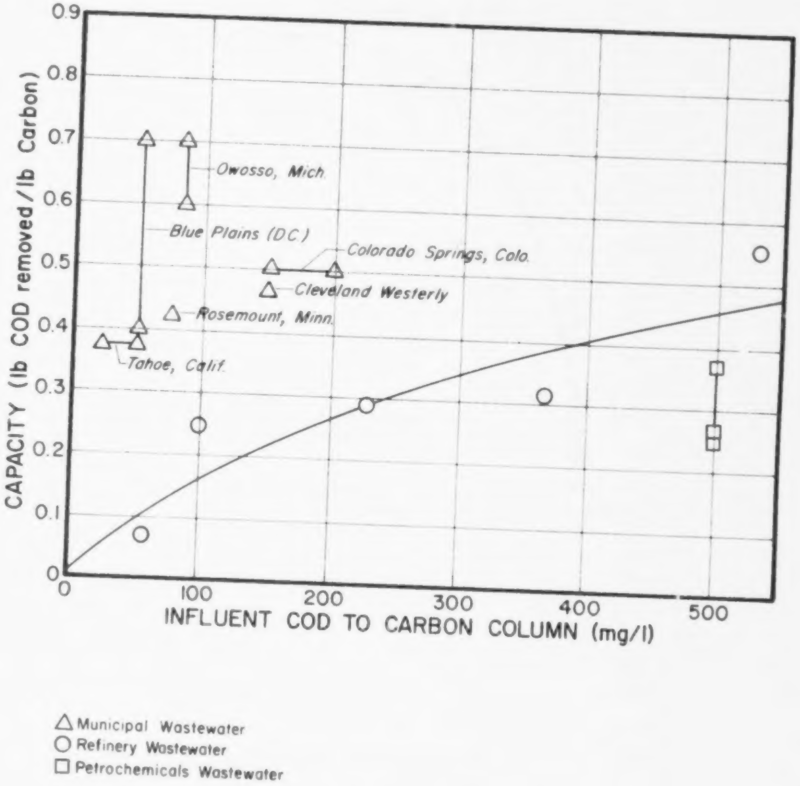


FIGURE 24

CARBON ADSORPTION CAPACITY FOR VARIOUS PLANTS



SECTION 2

Organic Compound Removal by Activated Carbon

CAUTIONS AND LIMITATIONS ON THE APPLICATION OF ACTIVATED CARBON ADSORPTION TO ORGANIC CHEMICAL WASTEWATERS

C. T. Lawson
and
J. C. Hovious
Union Carbide Corporation, South Charleston, West Virginia

OBSERVATIONS ON ACTUAL WASTEWATERS

Normal practice in assessing the feasibility of activated carbon adsorption is to first conduct batch adsorption isotherms with powdered activated carbon. These tests provide a relative indication of the amount of organic removal achievable by adsorption and the ultimate adsorptive capacity of the carbon. Unfortunately, these data are useful only in a relative sense - for comparing the relative merits of two different carbons, or for comparing the relative amenability of different wastewaters to adsorption. Isotherm data are not suitable for designing continuous granular carbon adsorption columns, since the dynamic effects and interactions in a continuous bed differ too greatly from the batch equilibrium situation in an isotherm.

Batch adsorption isotherms have been performed on many organic chemical bio-treated effluents and raw wastewaters of widely varying composition and overall organic concentration (COD or TOC basis). Figure 1 shows curves of percent organic removed vs. carbon dosage. It is obvious the amenability of these wastes to adsorption is rather wide - ultimate percentage organic removals vary from 45% to 90%. Even for those cases where 90% organic removal can be achieved by massive carbon dosing in batch tests, the organic removals achievable in continuous adsorbers are lower, often significantly so.

Comparing batch and continuous data for Plant A bio-treated effluent:

Ultimate % removal of TOC in isotherm test	90%
%TOC removal in continuous bed adsorber prior to breakthrough (1 bed vol/hr)	52%
%TOC removal before breakthrough (0.5 bed vol/hr)	64%

Not only was the organic removal predicted by isotherms not achieved, even in early stages of the column run with fresh carbon, but doubling the bed depth (halving the throughput rate) only raised the amount of TOC removal from 52 to 64%.

When batch adsorption data are plotted as log (wt. organic adsorbed/wt. carbon) vs. log (organic concentration remaining in solution), the Freundlich isotherm results - X/M vs. C_e. When the logarithmic plot is extrapolated to $C_e = C_o$ (the initial solution concentration), the resulting $(X/M)_{C_o}$ is called the "adsorptive capacity" of the carbon. These isotherm capacities are usually greater, often very much greater, than the ultimate adsorptive capacity exhibited by a granular adsorption bed at exhaustion. Typical examples from prior publications (1):

Wastewater	Adsorptive Capacity, gm COD/gm carbon	
	Isotherm	Column at Exhaustion
Plant A bio-effluent	1.3	0.26
Plant D bio-effluent	0.65	0.24
Plant G raw wastewater	0.075	0.05

Note that carbon had a very low adsorptive capacity for the constituents in Plant G wastewater.

It was further noted that increasing the carbon bed depth yielded not only the aforementioned limited increase in percentage organic removal, but also a diminished adsorptive capacity. Operating two beds in series until each bed was exhausted at an overall throughput of 0.5 bed vol/hr (1 BV/hr/column) showed:

	gm COD adsorbed/gm carbon	
	Col. 1	Col. 2
Plant A	0.26	0.17
Plant D	0.23	0.13

One may postulate that selective adsorption of the "more adsorbable" organics occurs in the lead bed. Not only that, when the first bed is exhausted, the second bed has little remaining capacity - implying that the "less readily adsorbed" species, which are initially removed in the second bed, block its further usefulness in removing "readily adsorbed" species (available when the first bed breaks through). This phenomenon is shown by the breakthrough curves of Figure 2. Just how "easily adsorbed organics" may be differentiated from "less readily adsorbed" species is a difficult question. The rate of adsorption at the carbon surface, the rate of diffusion within the carbon pores, and the ultimate capacity of the carbon for the adsorbates all play a part in affecting "adsorbability." In isotherm tests these factors are reflected in the measured adsorptive capacity and limiting percentage organic removal. In continuous columns they are reflected in the organic removal achieved and the rapidity with which organic breakthrough and exhaustion occur. The absence, or at least minimization, of diffusion limitations in powdered carbon isotherms can give a markedly different picture of "adsorbability," in terms of both extent and capacity, compared to the complex inter and intra particle diffusion phenomena which occur in a granular carbon bed.

PURE COMPOUND ADSORPTION STUDIES

Because of these observations of low percentage removals of TOC and COD, limited benefits of increasing carbon bed depth, and rather limited adsorptive capacities (in continuous columns), an extensive investigation was conducted (2) to quantify some aspects of "adsorbability" of specific organics. The effects of functionality, molecular weight and structure, aqueous phase pH, solubility, polarity, carbon surface structure, and adsorbate interactions were investigated. Column *vs.* isotherm comparisons were also made for several pure chemicals and simple mixtures.

In the first phase, 93 organic chemicals from 11 functional group families were subjected to single dosage adsorption tests.

Functional group families:
- Alcohols

Aldehydes
Amines and alkanolamines
Aromatics
Pyridines and morpholines
Esters
Glycols and glycol ethers
Ketones
Organic acids
Ethers and oxides
Halogenated aliphatics

Test conditions:
Initial compound concentration = 1000 mg/l (or solubility, if 1000 mg/l)
Carbon: 5 gm/l of powdered Westvaco Nuchar WV-G (surface area = 1100 m^2/gm)
Contact time = 2 hours

Typical graphs of adsorbate loading vs. molecular weight are shown in Figures 3, 4, and 5 for the alcohols, esters, and organic acids tested. The unfavorable effect of branching and the favorable effect of unsaturation can also be seen. Figure 6 is a "map" of percent of compound adsorbed (by 5 gm/l carbon) vs. molecular weight showing the regions which encompass all the experimental data.

Region A	Aromatics (including ring-substituted compounds)
Region B	General trend for aliphatic mono-functional oxygen and nitrogen-containing compounds
Line C	Saturated organic acid line, shown for comparison
Region D	Glycols, glycol ethers

Note that the aromatics, even those containing polar groups (-OH, $-NO_2$, -Cl) are quite amenable to adsorption, while the poly-functional oxygenated compounds (glycols, glycol ethers) are especially difficult to adsorb.

Qualitatively, it was concluded that adsorbability, as reflected in constant dosage tests, is favored by increasing molecular weight, aromaticity, and degree of unsaturation. Increasing polarity, solubility, branching, and degree of dissociation (for amines and organic acids) tended to severely limit the extent of adsorption.

The relative ease of adsorption for simple oxygenated organic compounds may be summarized as follows:
Number of carbon atoms 4
acids aldehydes esters ketones alcohols glycols
Number of carbon atoms 4 (straight-chain compounds)
acids aldehydes alcohols esters ketones glycols

The relatively low adsorption, in general, of compounds containing 4 carbon atoms in these tests is particularly noteworthy. The carbon dosage of 5 gm/l was a rather massive dosage - in a continuous column adsorber it would be equivalent to treating only about 24 gallons of wastewater per pound of carbon. This poor organic removal at high carbon dosage implies that carbon adsorption may have limited application to many organic chemical manufacturing wastewaters, from a cost-effectiveness viewpoint. Low molecular weight oxygenated organic compounds represent a very large fraction of the production volume in the industry.

In the next phase of the study, Freundlich adsorption isotherms were obtained on 1000 mg/l solutions of five different organic compounds (all containing four carbon atoms) using four different carbons at different aqueous-phase pH levels. Figure 7 shows that pH had a marked effect on the isotherm adsorptive capacity, $(X/M)_{C_o}$, for butyraldehyde and ethyl acetate. Data for Carbon A, Witco 517, are shown; similar trends were observed for other carbons. Gas chromatographic analyses indicated that, at acidic or basic pH levels, ethyl acetate was hydrolyzed into its less adsorbable (lower molecular weight) components. At elevated pH, butyraldehyde underwent an aldol condensation into a higher molecular weight (more adsorbable) component. More detailed discussion of differences between the carbons tested and the effects of carbon surface properties are contained in Ref. (2).

A potential problem in successfully applying activated carbon to multi-component wastewaters is indicated. It is not possible to select a pH level that assures maximal adsorption of all wastewater constituents. An acidic pH is required to facilitate adsorption of organic acids (to avoid ionization), near neutral pH favors adsorption of esters, while a highly alkaline pH is necessary to maximize adsorption of aldehydes.

MULTI-COMPONENT ADSORPTION STUDIES

Interactions in multi-component systems were examined in the third phase of the study by adsorption isotherm tests on binary and four-component mixtures. The results are shown in Table 1.

In a test (at pH = 7) of a butanol/ethyl acetate binary mixture (500 mg/l of each compound), the total adsorptive capacity was observed to be 0.237 gm cpds/gm carbon, while the sum of the two adsorptive capacities (at 500 mg/l initial concentration) from pure-component isotherms was 0.27 gm/gm. By gas chromatographic analysis of the residual solutions, the butanol adsorbate loading was 1.05 times the loading in a pure component test while the ethyl acetate loading was 0.76 times the pure component loading. Even though more ethyl acetate was adsorbed from the mixture, on a weight basis, than butanol (as expected from Figure 7), the interaction had a greater deleterious effect on ethyl acetate, in terms of using pure component data to predict mixture adsorbate loadings.

By contrast, in the butyraldehyde/MEK binary test, the total adsorptive capacity from the mixture (0.275 gm cpds/gm) was greater than the sum of the pure component values (0.270 gm/gm), more butyraldehyde (the "more adsorbable component") was adsorbed on a weight basis, and the ratio of mixture loading to pure component loading was greater for butyraldehyde, 1.28 vs. 0.60.

In both four-component mixture isotherms (Table 1), the total adsorptive capacity (0.29 and 0.225 gm/gm for Carbons A and C, respectively) was significantly less than the sum of the pure component capacities (0.575 and 0.312 gm/gm for Carbons A and C, respectively). Also, in the Carbon C test, less butyric acid was adsorbed than butyraldehyde or ethyl acetate, despite the previous pure component conclusion that acids are more adsorbable than other organic compounds.

Thus, while pure component adsorption data are useful in determining which waste streams are potential candidates for activated carbon treatment, the data cannot be used to quantitatively predict adsorption from multi-component systems.

CONTINUOUS vs. BATCH ADSORPTION STUDIES

In the fourth and final phase of the study, continuous column, granular carbon adsorbers were operated to exhaustion for comparison of ultimate capacities with isotherm capacities. Each column was operated at a throughput rate of 1 bed volume/hour. The feed concentration was 1000 mg/l in the pure component tests, 2000 mg/l (500 mg/l each compound) in the four component test (feed TOC = 1200 mg/l). The four component mixture was butyraldehyde, ethyl acetate, butanol, and butyric acid. In all cases, the ultimate capacity (at exhaustion) was less than that predicted by isotherms (83 to 89%).

	Adsorptive Capacity, gm/gm carbon		
Organic	Isotherm	Column at Exhaustion	Column at Breakthrough
MEK	0.160	0.132	0.103
Butyraldehyde	0.220	0.192	0.141
4-Component Mixture	0.170 (TOC)	0.151 (TOC)	0.124 (TOC)

Note that the usable capacity in a single-column system - the capacity achieved at "breakthrough," where significant organic concentrations appear in the treated effluent - is significantly less than indicated by the isotherms (64 to 72%). Figure 8 shows the experimental breakthrough curve for the four-component mixture.

A second important criterion when applying activated carbon in continuous beds is the amount of wastewater that can be treated before breakthrough (often called the "carbon dosage"). Breakthrough in full-scale practice (where the carbon is removed from service) would be set at the maximum organic concentration allowed by effluent standards. For purposes of discussion, breakthrough was set at the 95% organic removal level in these lab tests. Observed dosages were:

Test	Breakthrough "dosage" gal WW treated/lb carbon
MEK	12.7
Butyraldehyde	19.4
4-Component Mixture	12.4

Treating large volumes of wastewater at these inlet concentrations will, thus, lead to rather short service life (rapid breakthrough), even with the fairly ideal adsorption wavefront shape in Figure 8.

Hydraulic effects (channeling and axial dispersion) are a partial explanation for the failure of column adsorbers to achieve adsorbate loadings predicted by isotherms. The inherent differences between the static equilibrium attained in batch isotherms and the dynamic situation in a continuous column are also limiting factors, particularly when treating complex multi-component (4) wastewaters.

A recent paper (3) by Keinath has shown that competitive adsorption, even in binary solutions, can lead to chromatographic displacement effects in column adsorbers treating wastewaters of varying composition. In this situation, the weakly-adsorbed solute is retained by the carbon for a time and then is eluted as a rather concentrated "peak" upon prolonged contact with the feed wastewater. Keinath further showed that fluidized bed adsorbers are much less susceptible to this effect than more conventional packed beds - a finding that could have significant impact on adsorber design. Chromatographic displacement and related interaction effects are almost certainly key contributors to the diffused, spread-out adsorption wavefronts and fluctuating organic removals observed when treating multi-component organic chemical wastewaters of high component and concentration variability. The question of dynamic interactions and effects in multi-sorbate systems is an area where further research and development is sorely needed, not only to shed further light on which wastes can be efficiently treated by activated carbon adsorption, but also to ascertain how best to design and operate continuous adsorption systems to minimize the undesirable effects of interactions.

CONCLUSIONS

1. In pure component studies, specific organic chemicals have been shown to differ widely in their amenability to adsorption, depending on molecular weight, structure, polarity and solubility. Low molecular weight oxygenated organics are particularly difficult to adsorb efficiently.
2. The relative ease of adsorption of different functional group compounds can vary strongly with pH, depending on the chemical nature of the adsorbates. An optimum pH cannot be predicted for a multi-component wastewater of unknown or varying composition.
3. While pure component data could be used to predict binary adsorption capacity in isotherms fairly closely, a four-component mixture isotherm showed only about 60% of the adsorptive capacity predicted. Mutual solubility effects competition for adsorption sites, and inability to maintain a pH level optimum for all components contributed to this inability to extend pure component data to more complex mixtures.
4. While isotherm capacities were somewhat extrapolatible to continuous column behavior in pure component adsorption and simple mixture studies, such extrapolations have not proved to be possible with real wastewaters (complex mixtures), particularly with bio-treated effluents.
5. More importantly, the key parameters of interest in real wastewater treatment situations - percentage organic removal achievable and water volume treated per pound of carbon before breakthrough - cannot be predicted from isotherm tests.
6. The physical differences between an equilibrium adsorption situation in a powdered carbon isotherm and the dynamic, multi-component interactions in a continuous granular carbon bed are too great to permit prediction of column performance from isotherms or pure component data. The dynamic interplay of adsorption rates, pore diffusion rates, hydraulic effects, and pure component chemical properties in continuous columns is an area where further research efforts must definitely be applied.

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DISCUSSION

Frank Manning: Would you care to comment on how you would personally combine activated carbon with biological treatment together, which one is put first?

C. T. Lawson: Our normal thinking is that we would put carbon before biological treatment on specific streams where it has an application. In other words, on a stream say that's noxious for some reason but not biodegradable or perhaps biologically inhibitory, then we consider that a very good application for consideration of carbon. As a post-biological polishing step, it depends on how close we are to meeting a permit. I guess, if a little more treatment would get us to the permit then I would say a tertiary carbon system might be justified. I don't think, and we are convinced of this fact, that you can simply add on a carbon system and make up for deficiencies in your biological system. If you are far away from meeting a permit, the first think to do is make the bio-system work. Then if you need carbon to close the gap and it is effective in doing so, put it on; but I don't think that carbon can ever be considered as a prescription for a poorly operated treatment system.

Sterling Burks: Have you performed any studies on absorption of trace heavy metals? I know this question was asked of Davis Ford.

C. T. Lawson: No, we haven't.

Milton Beychok: As you know, I have congratulated you once before because I think it is long overdue that someone brought some science to this field. If we look at the data you have given us this morning, the isotherms in thermodynamic terms, the isotherms are really equilibrium. Your column data telling us you can't approach that equilibrium the way you think you should and that involves kinetics, and if we look again and make an analogy between that and other refining processes and what has been done in improving kinetics and the approach to equilibrium through catalysis. Do you intend or do you know of any research going on this pretreatment of carbon, trying to do something to improve the kinetics as well as perhaps making kinetic models and seeing what you can learn?

C. T. Lawson: Well the question of pretreating carbon, I really don't know of any work that is going on. It seems to be the kind of thing that the carbon vendors would be interested in and they are pretty competitive and closed-mouth fellows; they don't tell you much about what they are doing. There is some potential here, I would say, for tailoring carbons through pretreatment or through activation processes; but it is not being really studied much to my knowledge. On the question of developing a diffusion model or a kinetic model, there is quite a bit of academic interest I think in doing this. The only papers that I have seen are really for binary systems and that is not of too much interest in a practical application sense. I know Dr. Keinath at Clemson University and Dr. Weber at the University of Michigan have done some work in this modelling area.

Anonymous: It just seems to me from what we all know that the regenerated carbon behaves differently than the fresh carbon and you showed us today percentage wise some remarkable differences between two different carbons, that it would be a fruitful area for research work whether it be on the part of Union Carbide or the carbon manufacturer.

C. T. Lawson: Yes, I don't really want to give a commercial for anybody, but I will say that Witco's carbon in the studies we looked at performed quite well, very good carbon. I think there has been a lot of reluctance over the years to use anything but bituminous coal carbons because its "sturdier, more rugged, easier to regenerate, not as friable as the other carbons." Looking at waste treatment with some of the speciality carbons, coconut-shell carbons, has shown some pretty good results, - a little bit better than bituminous coal carbons. But when you talk about 75-85¢ per pound for carbon, it is really out of the question for large volume waste water treatment.

Nick Sylvester: You mentioned at the end of your talk that you have done some more research that you have not reported on and you also mentioned this apparent chromatographic type phenomena in the columns. Have you done more work on that and are you going to report that?

C. T. Lawson: That is what we have tried to do, we have tried to take a column and take samples down through the column at different times and see just where specific compounds end up in the column on a dynamic basis, to see if there is some way that you can predict when something is going to be spit out as a big eluted peak, and I hope that data will be in shape for the Cincinnati paper.

Dave Skamanca: Davis Ford mentioned that if you are going to put in an activated carbon system, you are really better off with biological system in front of it to decrease the loading and apparently improve the performance of the carbon. But as you decrease the loading, the pounds in the concentration to the activated carbon system, you also decrease the isotherm data, you don't get as good a loading on the activated carbon. Are you getting ahead of the game in most of these systems by trying to remove more of these pounds up stream with a carbon, are you gaining on the problem, are you just staying even so to speak?

C. T. Lawson: My own opinion is that the kind of capacities that you see in isotherm tests are really an interesting qualitative observation, but they have no practical significance. Anything you can take out before the carbon column by reasonable treatment means, I think is worthwhile. From what we have seen, running continuous column systems, this 25% or so by weight absorptive capacity (on a COD basis) to petrochemicals seems to be a pretty real number and relatively independent of the feed concentration in continuous systems for the wastes we have examined thus far. The fact remains that isotherm capacities obviously do vary strongly with concentration, you can go up and down. We really see no way to relate that to a continuous system. We use our isotherm data just for relative comparison of one waste water to another and one carbon to another; we don't use it in a quantitative sense at all.

BIOGRAPHY

Cyron T. Lawson is a Project Scientist in the Water Quality Development Group of Union Carbide's Chemicals and Plastics Division, Research and Development Department. He holds the B.Ch.E. and M.S.Ch.E. degrees from Georgia Institute of Technology. He has taught graduate courses in water and wastewater treatment as an Adjunct Instructor at the West Virginia College of Graduate Studies. Cyron is a Registered Professional Engineer (Chemical) in West Virginia and is a member of the AIChE and its Environmental Division.

Joseph C. Hovious is a Group Leader/ Technology Manager in the Research and Development Department of Union Carbide's Chemicals and Plastics Division. Mr. Hovious is an M.S. Environmental Engineer from the University of Illinois. He teaches graduate courses at the West Virginia University College of Graduate Studies. He is a member of the WPCF, AWWA, and a Registered Professional Engineer in West Virginia.

TABLE 1 "COMPARISON OF MULTI-COMPONENT ISOTHERM DATA WITH SINGLE COMPONENT DATA"

	Equilibrium Carbon Loading in Mixture Test g cpd/g carbon (a)	Equilibrium Carbon Loading in Single Component Tests, g cpd/g carbon (b)	Fraction of Single Component Equilibrium Loading from Mixture (c)
Mixture 1 - Carbon A			
Butanol	0.116	0.110	1.05
Ethyl Acetate	0.121	0.160	0.76
	0.237	0.270	
Mixture 2 - Carbon A			
Methyl Ethyl Ketone	0.063	0.105	0.60
Butyraldehyde	0.212	0.165	1.28
	0.275	0.270	
Mixture 3 - Carbon A			
Butyraldehyde	0.072	0.165	0.44
Ethyl Acetate	0.075	0.160	0.47
Butanol	0.031	0.110	0.28
Butyric Acid	0.112	0.140	0.80
	0.290	0.575	
Mixture 3 - Carbon C			
Butyraldehyde	0.072	0.080	0.90
Ethyl Acetate	0.066	0.080	0.83
Butanol	0.023	0.068	0.34
Butyric Acid	0.064	0.084	0.76
	0.225	0.312	

(a) Compounds each initially present at 500 mg/l. Mixtures 1 and 3 dosed at 1 gm carbon/liter and Mixture 2 at 2 gm carbon/ liter. Equilibrium loadings $(X/M)_{C_o}$ are calculated from total TOC loadings and chromatographically determined fractional compositions of removed material.

(b) Equilibrium loadings measured at C_o of 500 mg/l.

(c) Calculated by dividing the equilibrium loading of the individual components in the mixture by the single-component equilibrium loading.

FIGURE 1

ACTIVATED CARBON TREATMENT OF BIOLOGICAL EFFLUENTS
BATCH ADSORPTION ISOTHERM TESTS

C_o = initial COD (or TOC) concentration before carbon treatment

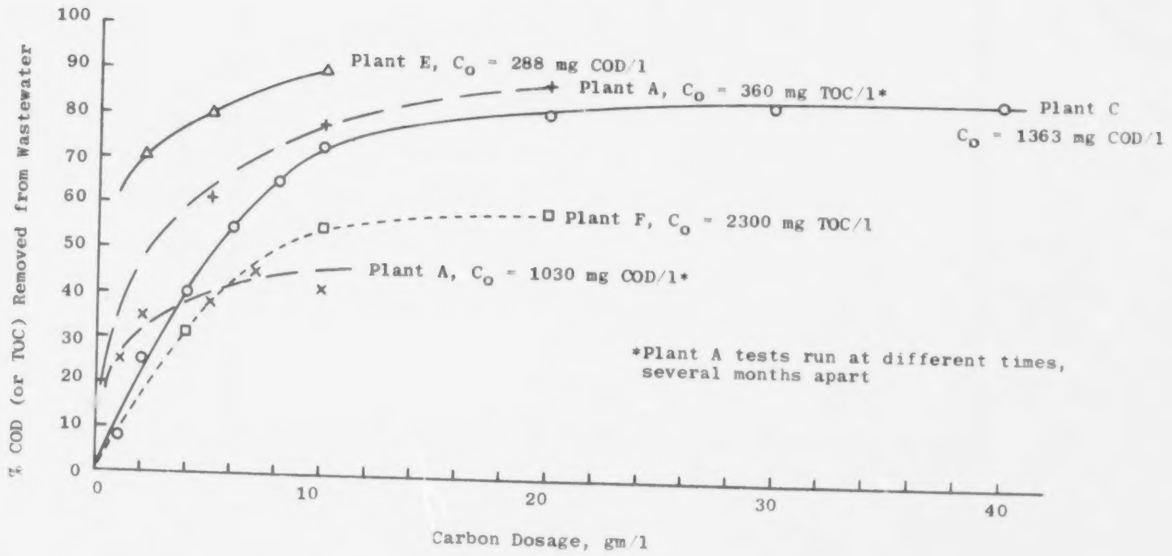


FIGURE 2

BREAKTHROUGH CURVE FOR PLANT A BIO-TREATED WASTEWATER

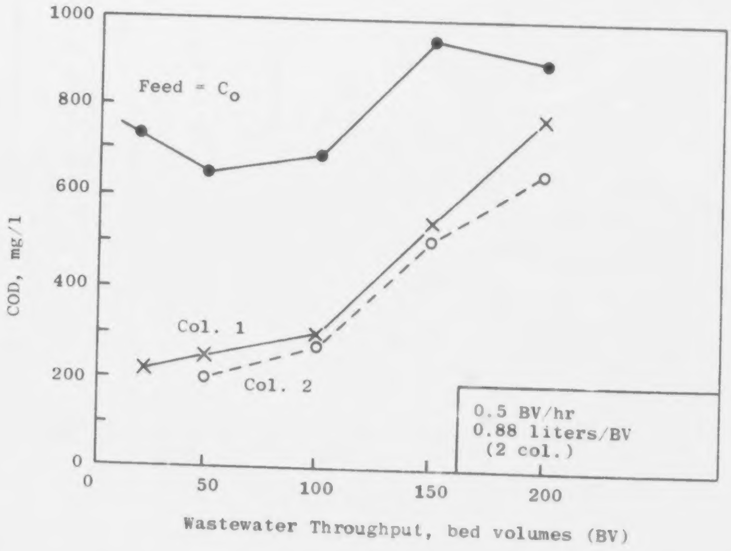


FIGURE 3

EFFECT OF MOLECULAR WEIGHT ON AMENABILITY OF ADSORPTION OF ALCOHOLS

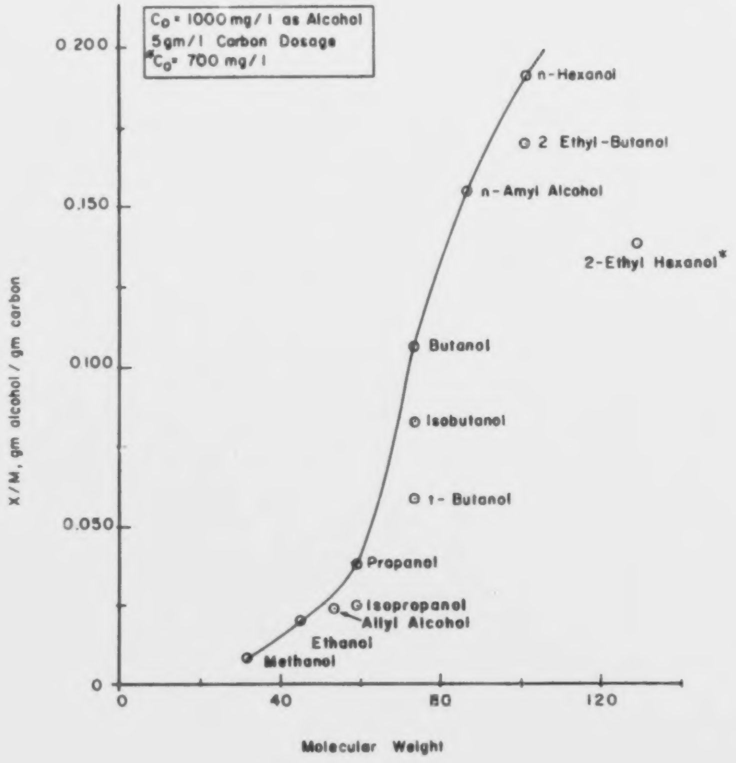


FIGURE 4

EFFECT OF MOLECULAR WEIGHT ON AMENABILITY OF ADSORPTION OF ESTERS

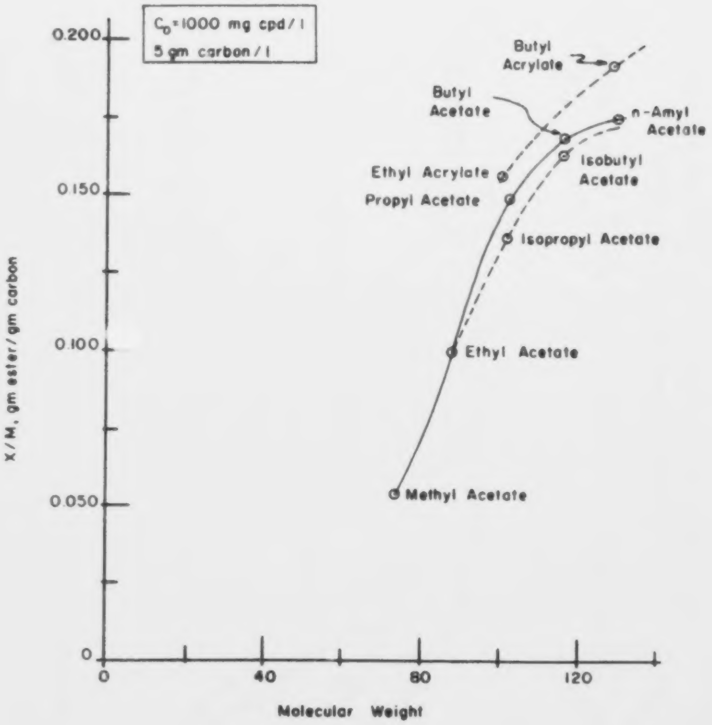


FIGURE 5

EFFECT OF MOLECULAR WEIGHT ON AMENABILITY OF ADSORPTION OF ORGANIC ACIDS

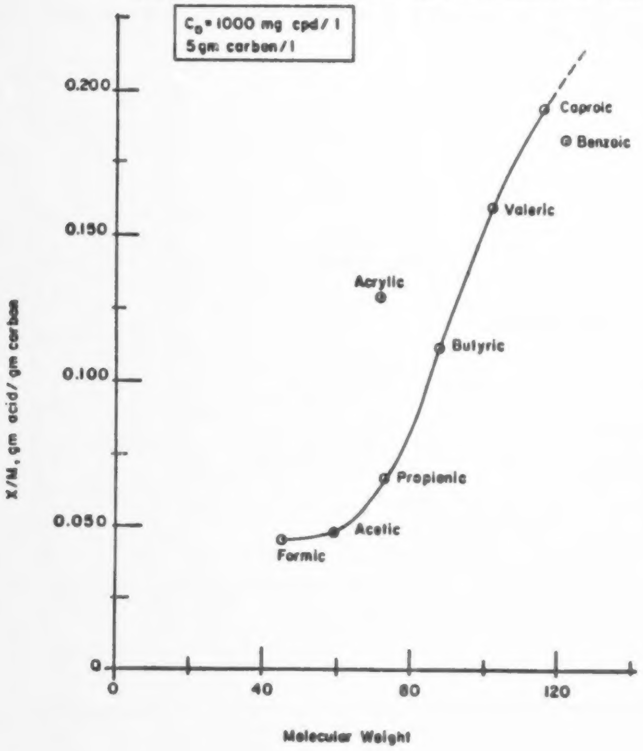


FIGURE 6

PERCENT OF COMPOUND ADSORBED VS. MOLECULAR WEIGHT FUNCTIONALITY EFFECTS

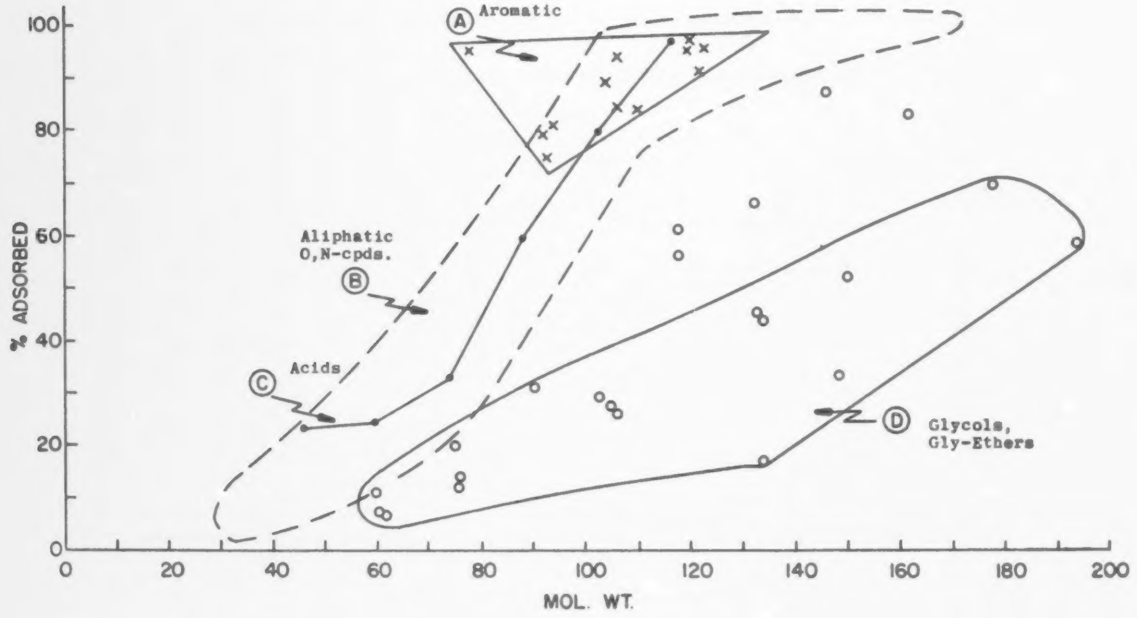


FIGURE 7

pH EFFECTS ON ADSORPTION REMOVALS OF SELECTED ORGANIC COMPOUNDS WITH CARBON A

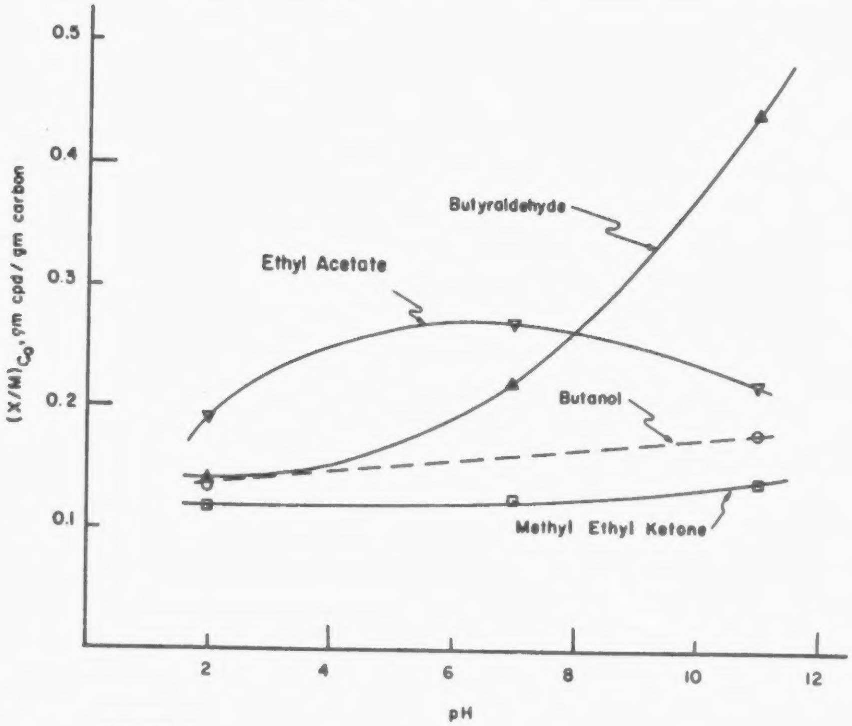
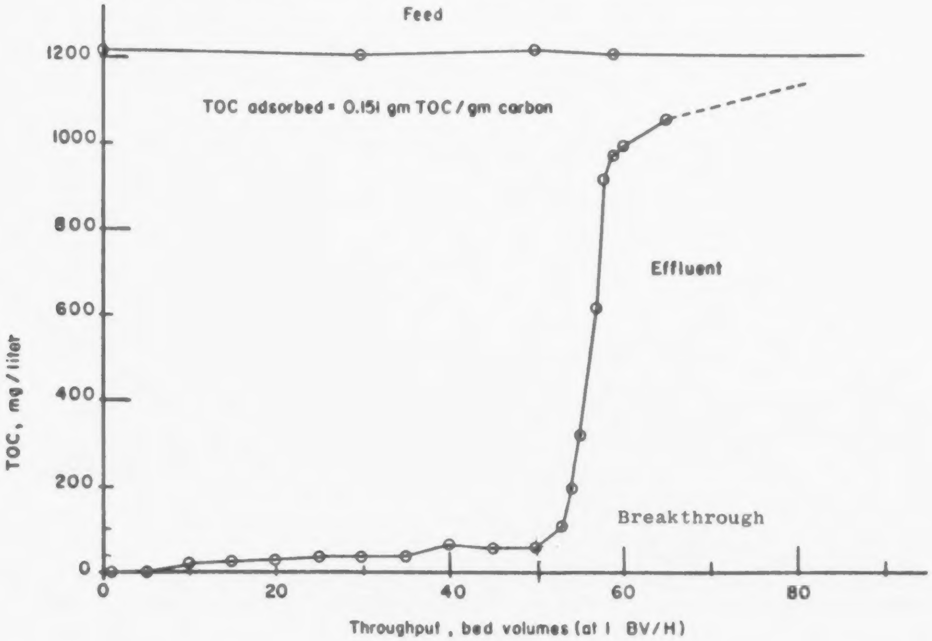


FIGURE 8

BREAKTHROUGH CURVE FOR ACTIVATED CARBON ADSORPTION OF A FOUR-COMPONENT MIXTURE IN A CONTINUOUS SYSTEM



ORGANICS REDUCTION THROUGH ADD-ON ACTIVATED CARBON AT PILOT SCALE

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ABSTRACT

The current wastewater BATEA model for the petroleum refining industry is the treatment sequence: activated sludge, mixed-media filtration, activated carbon. In an effort to develop data to assist in evaluating the model for specific organic compounds, the EPA (Ada, Oklahoma) entered into an Interagency Agreement with ERDA (Argonne National Laboratory) in January 1975. In cooperation with API, a .25 GPM pilot test was conducted at the SOHIO Refinery in Toledo, Ohio. Argonne followed with GC/MS analysis of samples collected across the treatment system to identify specific organics which are treatable versus those which pass-through (refractories).

The EPA's involvement included: the mobile pilot plant, refinery selection, conduct of the field study, sample preparation, and reporting. Argonne's analytical results showing a small overall reduction in organics by mixed-media filtration and a large reduction by carbon adsorption are discussed.

INTRODUCTION

In January 1975, the EPA (Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma) entered into an Interagency Agreement with ERDA (Argonne National Laboratory, Chicago) to develop data to assist in evaluating the performance of the BATEA model in the Development Document of 1974 (1). Since that time the BATEA regulations (and hence the BATEA model) have been remanded by a ruling of the 10th Circuit Court on the petition for revision of the guidelines by the API (2). However, the requirements for reconsideration and reissuing of guidelines as stipulated in the ruling, together with the mandates in PL-92-500 (Sec. 301. d.) (3), and the Settlement Agreement between EPA and NRDC (4), are added incentive to complete the work funded through this Interagency Agreement.

The proposed BATEA model was fixed bed carbon adsorption added onto the BPT model, which is biological treatment followed by granular media filtration. The specific treatment train selected for study was activated sludge, mixed-media filtration, and granular activated carbon. The performance criterion was to be the reduction of major organic compounds identified in the influent to the biological treatment system. Pursuant to the agreement, Argonne would perform qualitative organics analyses on samples provided by EPA. Pilot-scale filtration and carbon adsorption would be applied to the final effluent from a full-scale refinery treatment system. The results would serve as guidance for determining the need for larger-scale study and would not be used in predicting the performance of a full-scale add-on carbon system.

Refinery Selection

Considerable time was allocated to refinery selection, as there was sufficient funding to study only one refinery. Repeated discussions and meetings were held with members of the API's W-20 Task Group to arrive at a "representative" refinery. It was agreed to acquire permission from a Class B refinery whose final effluent quality met BPT, with the possible exception of suspended solids. Other criteria would include intake water quality and variability, refinery turnaround plans, and final effluent quality, raw waste loading, and hydraulic detention times typifying the activated sludge process at a Class B refinery.

Agreement was reached in September 1976, to conduct the study at SOHIO's Toledo refinery. This is a Class B refinery (crude topping and catalytic cracking) with coking, having a crude capacity of 120,000 BPSD. The treatment train at that time consisted of the API Separator, dissolved air flotation (DAF), activated sludge (extended aeration) having 16-18 hours detention, and final clarification. The final effluent quality routinely satisfied BPT requirements with the exception of suspended solids. The refinery treatment system returned to steady state in November 1976, following a 1-month turnaround period.

The Pilot Study

A 30' EPA mobile trailer was transported to Toledo and positioned near the final clarifier. Facilities aboard the trailer included 6" I.D. glass columns for filtration and carbon adsorption (Figure 1), a TOC analyzer for monitoring organic carbon breakthrough, pumping and distribution capability, and sampling gear. The sampling equipment, pumps, and distribution lines were fabricated and installed such that the only materials in contact with water moving through the pilot treatment system were stainless steel, glass, Teflon, and polypropylene (Figure 1). Sampling points aboard the trailer were: 1) SOHIO's final clarifier effluent, 2) pilot mixed-media filter effluent, and 3) pilot carbon column effluent (Figure 2). The two remaining sample points were SOHIO's intake water and DAF effluent (Figures 3 & 4). These five points were sampled and iced on 4-hour intervals for 24-hour compositing over a consecutive 4-day period. During the study, there were no significant changes in recorded flows through the full-scale treatment system, as measured by the hourly biofeed pumping rates.

Two parallel down-flow mixed-media filters were utilized such that while one was operating for 24 hours, the second, having been backwashed, was ready for use the next day (Figure 5). Figure 2 shows the configuration of the filtering bed: anthrafilt, sand, and gravel. The sand used has an Effective Size = 0.2 mm and a Uniformity Coefficient = 4.5. Backwashing was accomplished by alternately pulsing with air and pumping carbon column effluent.

Two up-flow carbon columns (Figure 6) were packed as shown in Figure 2 and operated in series to achieve a total bed depth of 6 feet. A constant flow rate of 0.25 gpm was maintained, giving a residence time in the carbon bed of 36 minutes. The carbon used was Calgon's Adsorption Service Carbon. Calgon's analyses of a sample from the lot used at Toledo gave these results:

Apparent Density (gcc): 0.51
Molasses Number: 282
Iodine Number: 821
Sieve Result (mesh): 8x40

Attention was given to decontaminating material coming in contact with water samples. All glassware was cleaned by firing, maintaining 550°C for 1-hour. Sample bottle caps contained Teflon liners which had been cleaned by Soxlet extraction with methylene chloride--the solvent later used in the laboratory for extracting the organics from the water samples.

Each daily composited sample set was transported in ice chests to Detroit for air shipment. The samples arrived at RSKERL in Ada within 9 hours of final compositing in Toledo.

Laboratory Phase

Performance of the full-scale biosystem and the add-on filtration/carbon train for the common wastewater parameters is shown in Tables 1 & 2. Some values are reported as less-than (<), reflecting lower limits of detectability as a function of the sampling and analytical protocol.

Following the field study, the remaining responsibility of EPA was the preparation of the composited water samples for organics analysis by Argonne. This involved a tedious liquid-liquid extraction sequence using methylene chloride. Again, all glassware was fired for organics decontamination. A major problem was emulsion formation, requiring emulsion breaking and phase separation by various techniques. Each organic extract was dried by passing through anhydrous sodium sulfate and the solvent was stripped, resulting in 1-ml of concentrated extract which was sealed in a glass ampul. A period of 9 man-hours was involved in preparing each sample to the ampul stage; there were 20 samples requiring this preparation.

Gas-Chromatography/Mass-Spectrometry (GC/MS)

The samples supplied to Argonne for analysis consisted of 1 mililiter methylene chloride solutions of the acid, base, and neutral fractions composited over the 4-day sampling interval.

Analysis of the specific organics in these fractions was performed on a Hewlett-Packard Gas Chromatograph/Mass Spectrometer equipped with a data system and such peripheral equipment as a Zeta plotter and hard copy unit. Capillary columns were used in the gas chromatograph. These columns allow considerably greater separation and resolution of the organic components in a sample than do standard packed columns. Capillary columns also provide increased sensitivity and drastically reduced background from column bleed in the mass spectra. Also as opposed to typical GC/MS operation, no separator was used to remove the carrier gas. The outlet of the capillary column was connected directly to the source of the mass spectrometer and, therefore, there could be no discrimination in the amount of each component reaching the mass spectrometer. That is, assuming that the individual components in the mixture are not lost in the column, the effluent of the column and the amount of these components reaching the source of the mass spectrometer is a true representation of the quantities of compounds injected on the column. Finally, a Grob-type injection system was used in place of the inlet splitters typically used with capillary columns. The Grob system avoids the loss of large amounts of samples and the discrimination, typically found in split systems, of components of the mixture. It permits the analysis of minute concentrations of the specific organics present.

Figure 7 is a capillary column GC/MS total ion chromatogram of the neutral fraction of the dissolved-air-flotation effluent. It can be seen that there are over one hundred peaks or components in this fraction and that many of the components are present in minute quantities; that is, of the order of 200 ppt of the original water sample, assuming 100% extraction efficiencies. It was found that the organics in this neutral fraction of the DAF effluent were predominantly n-alkanes, alkyl benzenes, alkyl naphthalenes and polynuclear-aromatic hydrocarbons.

The activated sludge treatment system reduced the concentration of the organics in the DAF effluent by nearly 98%, as shown in Figure 8. It can be seen from the graphs that the peak height of several of the peaks in the FC effluent is approximately one-twentieth those in the DAF effluent, indicating there is approximately a twenty-fold reduction in pollutants by the activated sludge process.

Further reductions in organics were accomplished by the multi-media filter and the activated carbon column as shown in Figure 9. The concentration of the largest peaks of the compounds refractory to the add-on treatment system is of the order of 10 ppb. The percent reduction of the major classes of organics by the multi-media filter and the activated carbon column is as follows:

Compound	% Reduction
Alkanes	70-98
Alkyl Benzenes	35-90
Indenes	50-60
Indanes	76-96
Naphthalene	66
Alkyl Naphthalenes	65-90
Anthracene/Phenanthrene	86-93
Alkyl Anthracenes/Phenanthrenes	89-98
Other PNAs	96-98

It can be seen that there is generally greater than fifty percent reduction in these classes of organic compounds.

Work has not yet been completed on the acid and base fractions. Results will be available in a few months. The results of this study will be published as EPA and Argonne reports and as such will be available to the public.

It is expected that sufficient funds will be forthcoming in the next fiscal year to search and manipulate the data stored on disc for those consent-decree organics that may be present in these samples.

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ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance of the Calgon Corporation relating to activated carbon and the efforts of the API's Water Quality Committee and W-20 Task Group in arriving at a suitable refinery. We wish to thank Messrs. C. Tome, L.S. Van Loon, and J.H. Walters for assistance in the wastewater sampling program and Mrs. C.S. Chow for help with the GC/MS analyses. Most important, the study would not have been possible without the cooperation of SOHIO personnel at the refinery in Toledo and in the Department of Environmental Affairs in Cleveland.

DISCUSSION

Peter J. Foley, Mobil Oil: Would you comment on the contributions of the filter and the carbon columns in reducing organics?

Raphaelian: Although I do not have the exact numbers at hand, it appears to me that the multi-media filter had little or no effect on the concentration of organics whereas the activated carbon removed appreciable amounts of organics.

T. A. McConomy, Calgon Corp.: The naphthalene removal was only 66% as compared to more than 90% for other PNA's, why?

Raphaelian: These numbers are approximate figures based on the average of peak areas of individual components. Generally, one can say that those organics that have a long alkyl chain such as an alkane or an alkylated PNA are adsorbed on the carbon whereas parent PNA's are not. This is, of course, a crude approximation. We are still trying to get better gas chromatograms because all of these results are dependent upon how well you separate the compounds.

N. F. Seppi, Marathon Oil: Please comment on methylene chloride purification - also what about decomposition products from methylene chloride under basic conditions?

Pfeffer: Regarding the purity of methylene chloride, we relied upon the glass distillation procedures of the manufacturer (Burdick and Jackson). In addition, Argonne received a blank extract obtained by taking a high purity water and performing the acids, neutrals and basic extractions. This blank would also account for laboratory contaminations. I cannot offer any information about alkaline decomposition products.

Anonymous: Is there additional data from industry on the study at Toledo?

Pfeffer: I do not know. Both Exxon and SOHIO conducted parallel work to our own, presumably into the realm of GC mass-spec. We would entertain comparing notes with Exxon and SOHIO at some later date in order to validate what actually took place in Toledo.

Judith Thatcher, API: I noticed that the TOC of the influent water is very close to the TOC of the final effluent. Have you done any identification in the organics in the influent water to the refinery?

Pfeffer: We are looking at it, but haven't identified all the components yet.

Arthur J. Raymond, Sun Oil Co.: What phase was used on the capillary columns, and did you notice that your highly branched-chains were degraded much faster than the less branched? Also, was benzene degraded much faster than toluene and xylene?

Raphaelian: I don't understand what you mean by degraded.

Raymond: Did they decompose faster or disappear or reduce? Not in the column but in your system as you went from the influent water to the final clarifier. If you had percent reductions, which compounds went faster than others?

Raphaelian: I am still putting all this data together. However, I can say that it appears that the branched-chained alkanes, which were present in smaller quantities than the straight-chained alkanes, were not removed as well by the treatment system as the straight-chained alkanes. Because of the minute quantities of pollutants present, I am presently doing single-ion monitoring to try to get a better idea of the percent reduction across the treatment system.

Raymond: What phase did you use on a capillary column? What coating?

Raphaelian: For the work presented in this talk, OV-101 was the liquid phase and the columns were wall coated open tubular (WCOT) and not support coated open tubular (SCOT) capillary columns. It is difficult with OV-101 to get symmetrical peaks with polar compounds, that is, peaks without tailing. I used FFAP capillary columns for the acid and base fractions. By the way, we see a variety of alkylated phenols in the acid fraction.

Ed Sebesta, Brown & Root: I noticed that for TSS there is no decrease across the filter. Do you have any explanation for that?

Pfeffer: My only explanation is that considering the flow rate and sand specifications, the TSS coming from the final clarifier were such that the filter was ineffective. Also, at the 10 mg/l level, differences are probably within the experimental error of the test procedure.

BIOGRAPHIES

Fred M. Pfeffer holds the BA and MS degrees in Chemistry from the University of Cincinnati. He is currently a Research Chemist at the EPA's Robert S. Kerr Environmental Research Laboratory at Ada, Oklahoma.

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Leo Raphaelian holds the AB degree from Harvard University and the MA and a PhD degree in Chemistry from Yale University. He is currently Manager of Environmental Sciences, Energy and Environmental Systems Division at the Argonne National Laboratory, Argonne, Illinois.

Table 1. DAILY PERFORMANCE FOR COMMON WASTEWATER PARAMETERS

	MG/L INTAKE				MG/L DAF EFFLUENT				MG/L FC EFFLUENT			
	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4
Oil & Grease	<10	<10	<10	<10	22	33	21	22	<10	<10	<10	<10
Cyanide	<0.02	<0.02	<0.02	<0.02	0.19	0.25	0.31	---	0.16	0.12	0.20	0.10
Phenol	0.03	<0.01	0.03	0.01	320	260	520	450	0.02	0.01	0.04	0.02
COD	<15	18	<15	<15	122	172	154	154	49	50	51	44
BOD	<10	<10	14	<10	82	127	108	96	<10	15	21	24
TOC	19	19	17	15	39	56	72	60	22	29	27	17
TSS	35	29	11	<10	31	56	37	30	12	<10	<10	<10

	MG/L FILTER EFFLUENT				MG/L CARBON EFFLUENT			
	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4
Oil & Grease	<10	<10	<10	<10	<10	<10	<10	<10
Cyanide	0.16	0.15	0.20	0.10	<0.02	<0.02	<0.02	<0.02
Phenol	0.02	0.01	0.02	0.02	<0.01	<0.01	<0.01	<0.01
COD	42	38	51	44	<15	<15	<15	<15
BOD	<10	11	22	27	<10	<10	<10	<10
TOC	19	26	23	18	10	12	11	<5
TSS	<10	<10	12	12	<10	<10	<10	<10

Table 2. AVERAGE PERFORMANCE OVER 4-DAY STUDY PERIOD FOR COMMON WASTEWATER PARAMETERS

	MG/L INTAKE	MG/L DAF	MG/L FC	MG/L FILTER	MG/L CARBON
Oil & Grease	<10	24	<10	<10	<10
Cyanide	<0.02	0.25	0.14	0.15	<0.02
Phenol	0.02	390	0.02	0.02	<0.01
COD	<15	150	48	44	<15
BOD	<10	103	17	17	<10
TOC	18	57	24	22	9
TSS	21	38	<10	<10	<10

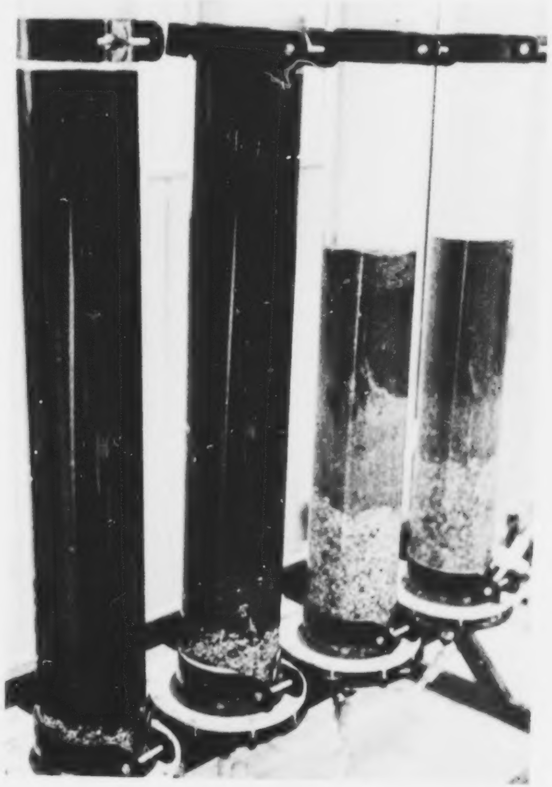

Figure 1. CARBON COLUMNS

Figure 3. SAMPLING POINT: PLANT INTAKE

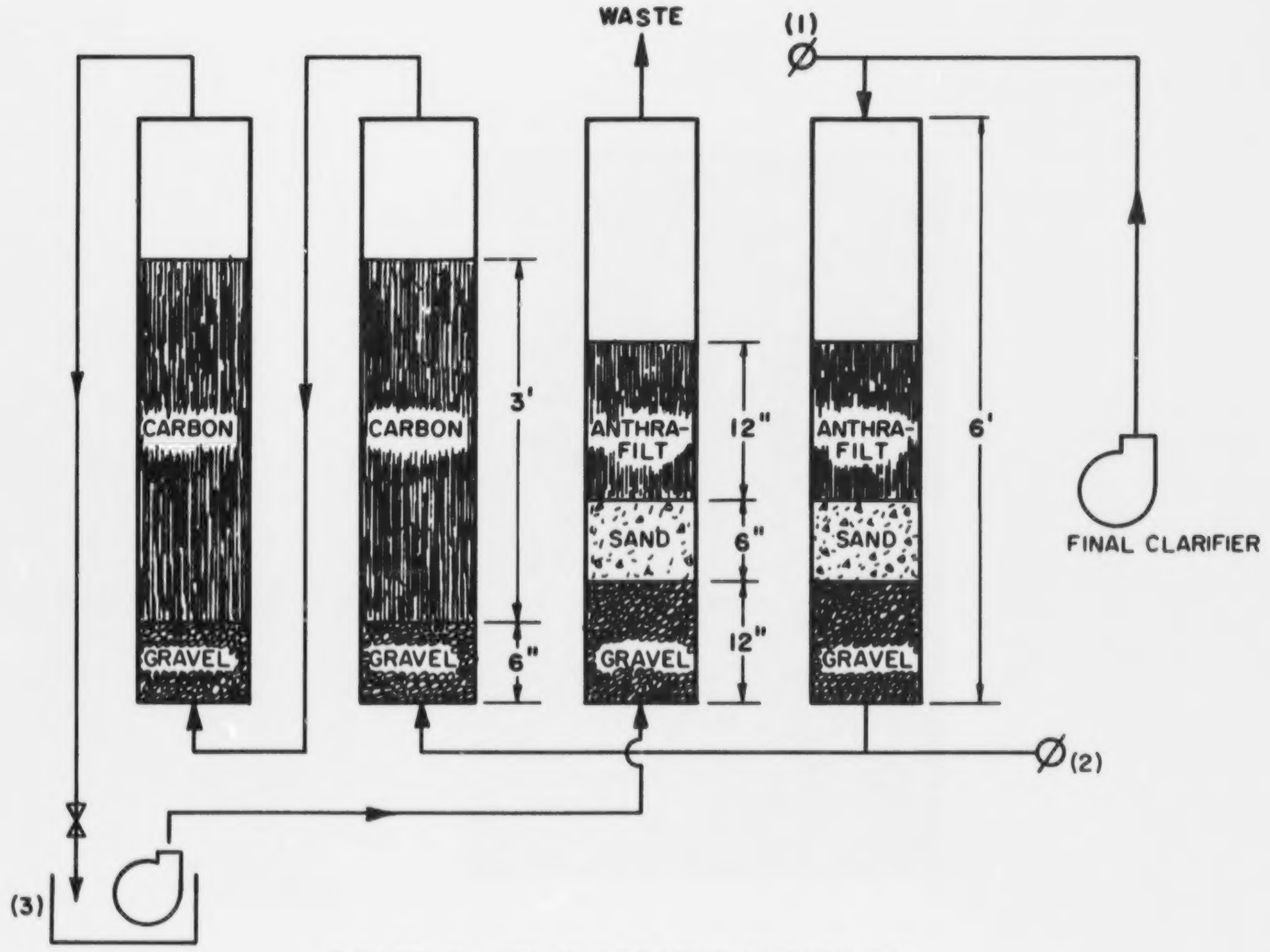
WASTE
(1)
Ø
CARBON
GRAVEL
CARBON
GRAVEL
3'
6"
ANTHRA-FILT
SAND
GRAVEL
12"
6"
12"
ANTHRA-FILT
SAND
GRAVEL
6'
FINAL CLARIFIER
Ø (2)
(3)

FIGURE 2 - PILOT TREATMENT FACILITY

Figure 4. SAMPLING POINT: DAF EFFLUENT

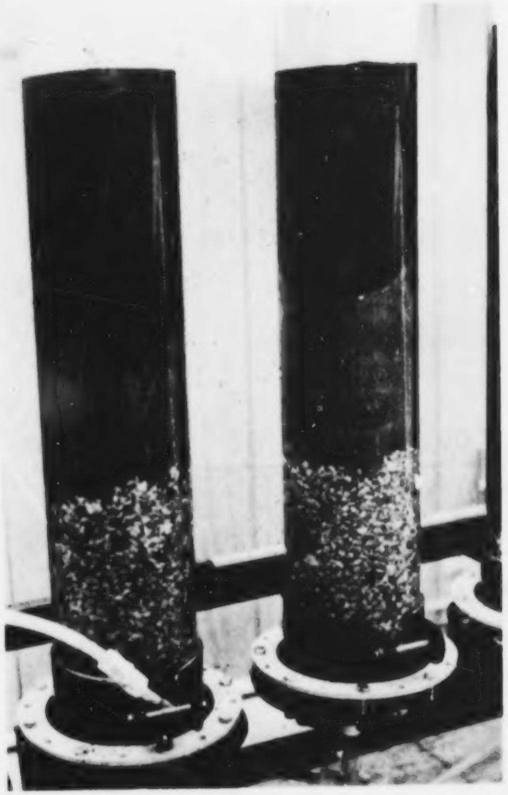

Figure 5. MIXED MEDIA FILTERS

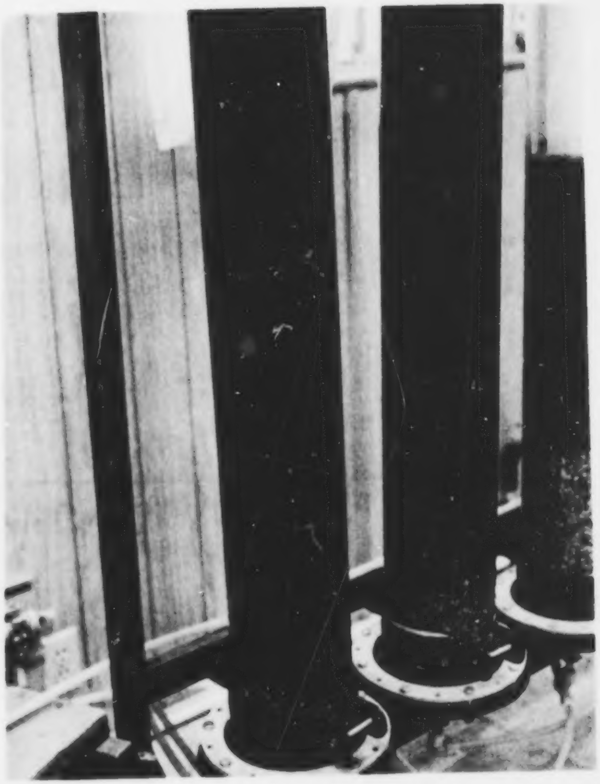

Figure 6. CARBON COLUMNS

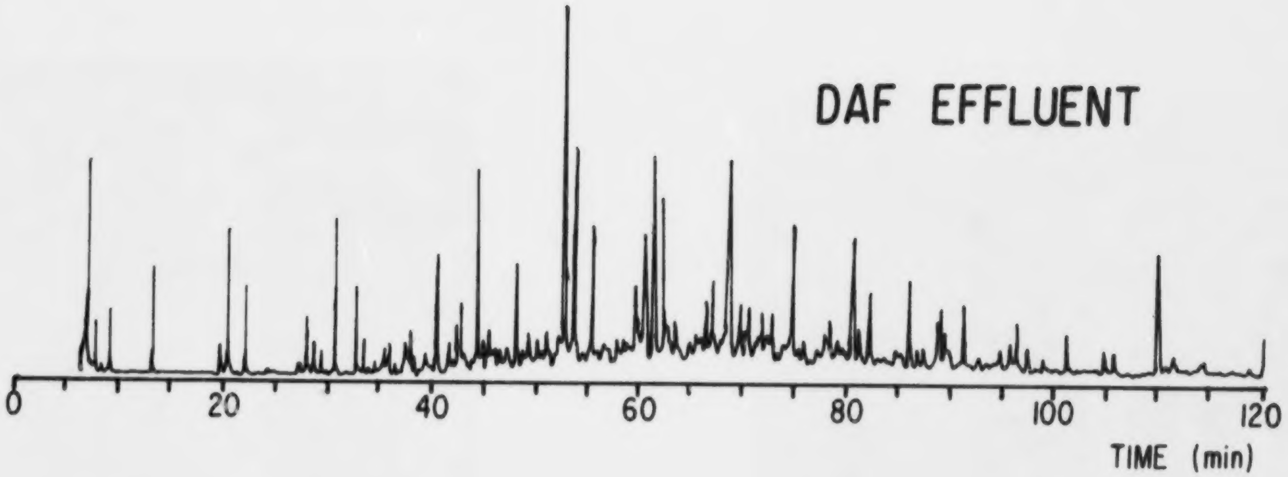

Figure 7. Total Ion Chromatogram of DAF Effluent (Neutral Fraction, Four-Day Composite)

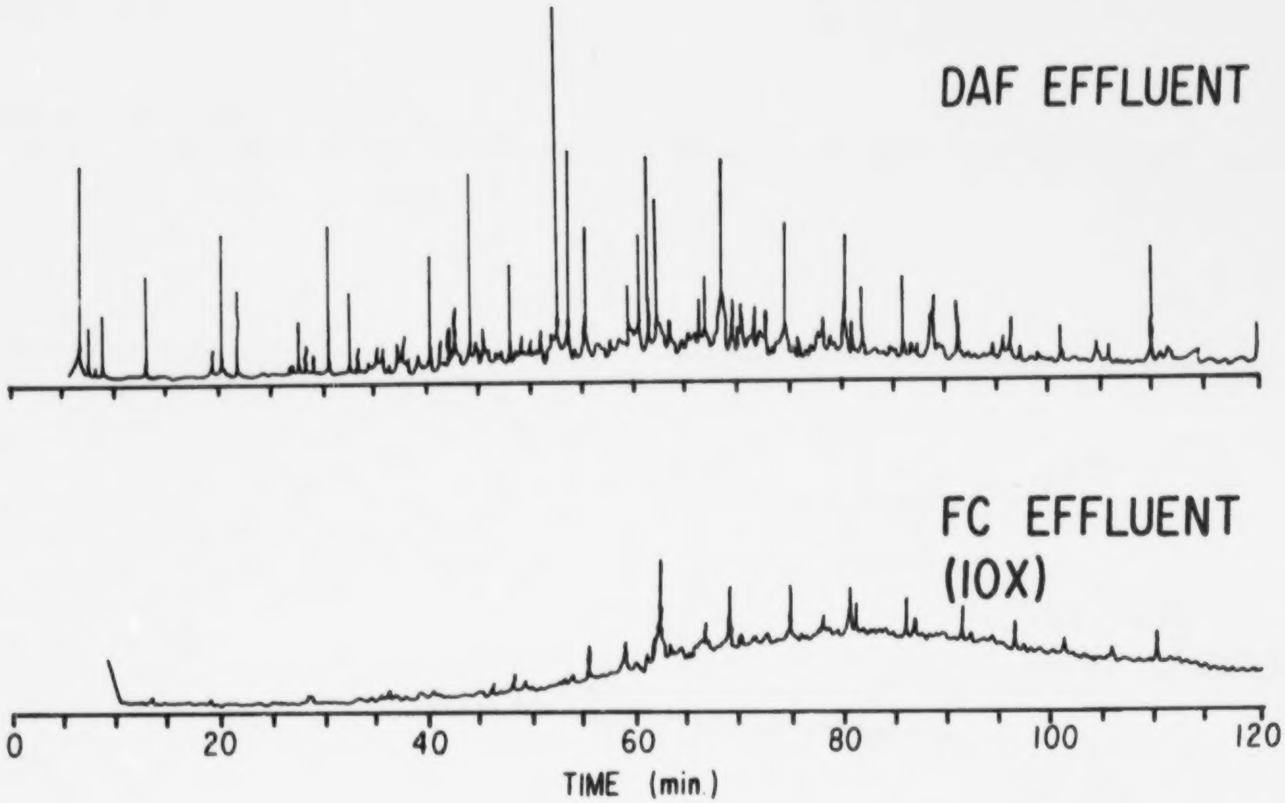

Figure 5. Total Ion Chromatograms of DAF Effluent and FC Effluent (Neutral Fraction, Four-Day Composite)

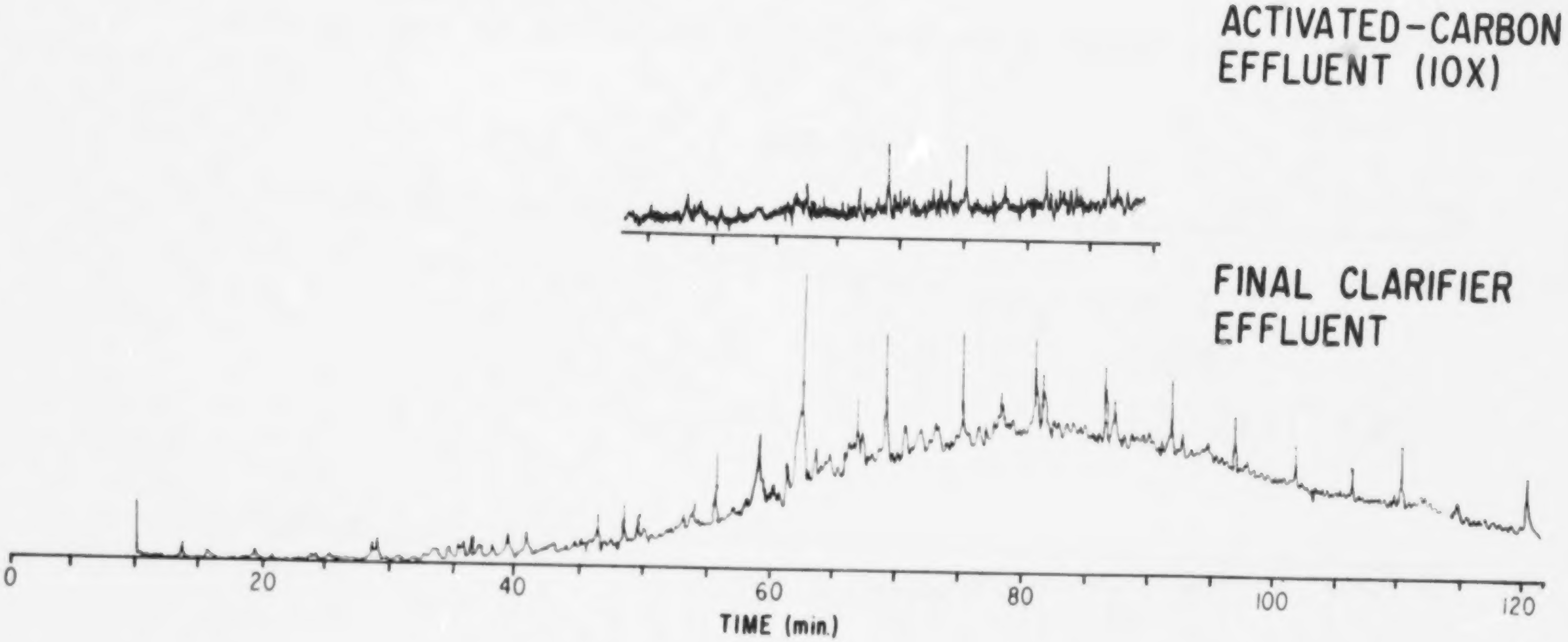

Figure 9. Total Ion Chromatograms of the Activated-Carbon and Final-Clarifier Effluents (Neutral Fraction, Four-Day Composite)

SECTION 3

Granular Activated Carbon Pilot-Scale Studies

"ACTIVATED SLUDGE ENHANCEMENT: A VIABLE ALTERNATIVE TO TERTIARY CARBON ADSORPTION"

Leonard W. Crame

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INTRODUCTION

In view of the possibility of more stringent 1983 BATEA (Best Available Technology Economically Achievable) effluent guidelines,[1,2,3,4] petroleum refiners are faced with the dilemma of an insufficient data base to determine the proper approach for making cost-effective improvements. The EPA previously proposed granular activated carbon adsorption after activated sludge treatment as BATEA technology; however, the current emphasis is to consider both effluent quality and the cost effectiveness of attaining the desired results. Two proposed approaches to BATEA technology are (1) increasing the sludge age (or mean cell residence time) of the activated sludge biomass to develop a more diverse population capable of assimilating biorefractory organics or (2) adding powdered carbon directly to activated sludge aeration basins. Both alternatives to tertiary carbon adsorption would require little capital investment and would lower operating costs.

Grutsch and Mallatt[5,6,7,8,9,10,11] have proposed that the best refinery end-of-pipe treatment for soluble organic removal should include pH control, equalization, optimized dissolved air flotation (DAF), and high sludge age (20-50 days) activated sludge treatment. High sludge ages (SA) require mixed liquor solids levels above conventional levels (5-10 days SA). These higher levels increase solids flux and must be considered in secondary clarifier solids loadings. Also high effluent TSS, despite less frequent sludge wasting, can result in a loss of mixed liquor solids.

Grutsch and Mallatt emphasize that optimized chemically-assisted DAF pretreatment (or comparable pretreatment) reduces the colloid charge (zeta potential) to maximize particle agglomeration for efficient flotation, and reduces the organic load on the activated sludge unit (ASU). Removing colloids normally present in raw refinery wastewater allows better bioflocculation and lower effluent total suspended solids (TSS) since most refinery colloids and biosolids have repelling negative charges. The microbial population could then acclimate to the biorefractory organics by producing enzymes which reduce these to simpler biodegradable substrates. Current reports from within the petroleum industry seem to indicate some benefits for increasing SA. Other investigators[12] have reported that high SA (low food/microorganism ratio) produces poor sludge settleability.

As a result of pilot studies at the Du Pont Chambers Works, Hutton and Robertaccio[13] were issued a U.S. patent[14] for the Du Pont PACT process.[15] The PACT process basically involves the addition of powdered carbon (or fuller's earth, etc.) to an ASU, usually in a range of 50-400 mg/l based on influent flow. Du Pont has reported[16,17,18] a number of advantages of the PACT process which include:

(1) color removal,
(2) stability against shock loadings,
(3) improved BOD removal,
(4) improved refractory organic removal,
(5) resistance to toxic substances,
(6) improvement in hydraulic capacity,
(7) improved nitrification (mainly in municipal wastes),
(8) foam suppression, and
(9) improved sludge settling and increased clarifier capacity.

A disadvantage of the PACT process is that the system can become very expensive if powdered carbon addition rates become high (hundreds of mg/l), even though powdered carbon is cheaper than granular carbon.

DeJohn and Adams[19,20,21] have developed a considerable amount of pilot study data on activated sludge-powdered carbon systems. They report significant enhancement in studies involving refinery and petrochemical wastewaters. DeJohn and Adams explain the powdered carbon enhancement mechanism as localization and concentration of oxygen and pollutant as the result of adsorption on carbon surfaces, resulting in a more complete biooxidation. The adsorption of biorefractory organics allows a longer residence time for these components in the system. Other researchers[22,23] have found similar improvements using activated sludge-powdered carbon systems and propose analogous enhancement mechanisms.

Rizzo[24] has reported a case history of a full-scale activated sludge-powdered carbon demonstration run at the Corpus Christi, Texas, Sun Oil refinery. Results included better system stability, reduction of foaming, resistance to upset conditions, lower effluent suspended solids and clearer effluent, and improved organic removal. These improvements were achieved by maintaining only a 450-mg/l powdered carbon reactor concentration with a 10-mg/l powdered carbon dosing requirement. The shortcoming of this investigation was that a parallel control could not be run simultaneously and most improvements reported could possibly have been attributed to better clarification.

The merits of powdered carbon enhancement have been further confused with the more recent development of several types of powdered carbons with significantly different properties.

SCOPE OF WORK

1. Objective

The objective of this study was to determine if the relatively simple process changes of increased sludge age or the addition of powdered activated carbon in conventional refinery activated sludge systems can significantly enhance the removal of organic wastewater contaminants to achieve or approach the level of proposed BATEA (1983) technology more cost effectively than the addition of granular activated carbon contactors to BPCTCA (1977) technology.

2. Procedures

In Part I of this study, five completely-mixed (15 gal) ASU's were operated in parallel with identical 18-hr retention times and 300-gpd/sq ft clarifier rise rates. A sixth ASU was run as a second-stage unit with the same 18-hr retention time (Figure 1). All biological reactors were located in a temperature controlled room in an attempt to dampen influent wastewater temperature variations and control biological reactions at about 85 F.

ASU's A and F served as controls, simulating conventional refinery units with a 0.3 lb TOC/lb MLVSS-day organic loading. Separate controls were run to determine the effect of optimized pretreatment on activated sludge treatment and tertiary carbon adsorption. Equalized (24-hr) and pH-controlled refinery wastewater was pretreated by dual-media (sand-anthracite) filtration (4.6 gpm/sq ft) and a chemically assisted DAF unit (1.5 gpm/sq ft) prior to control ASU's A and F, respectively. The optimized DAF pretreatment neutralized the negatively charged colloids, thus facilitating their removal and producing a bio-unit feed that contained essentially only soluble organics. Sodium phosphate (monobasic) was added to the filter and DAF unit effluents for a minimum TOC:phosphorus ratio of 100:2 to assure a proper nutrient level. Effluents from ASU's A and F were continuously filtered through a dual-media (sand-anthracite) tertiary filter for TSS removal before passing through a series of four granular activated carbon contactors to simulate proposed 1983 BATEA technology.

ASU's B, C, and D treated optimized DAF effluent with sludge wasting calculated for a 50-day biological SA. A commercially available, conventional-surface-area, powdered carbon[25] (designated PC-C) was added daily to ASU C to maintain a 500-mg/l reactor operating level. Similarly, PC-H, a high-surface-area powdered carbon,[26] was added to ASU D to investigate its enhancement capabilities.

ASU E was also operated at a 50-day SA treating ASU B effluent to determine if there was any benefit to ASU staging.

In Part II of this study, the second-stage ASU E was placed in parallel with other ASU's treating the DAF unit effluent as shown in Figure 1 and redesignated as ASU G. PC-H was added to ASU G to maintain a 2500-mg/l operating level while powdered carbon levels were increased in ASU C and D to 1000 mg/l.

Effluents were collected daily, Monday through Friday, as grab samples. Grab samples were taken in lieu of composites for convenience since the pilot unit treatment scheme contained significant equalization. Samples from the equalization basin, biological reactors, and carbon columns were filtered with Gelman type A/E glass fiber filters to give the soluble contaminant (TOC, COD, S=) level. Glass fiber filters were used instead of 0.45-micron filters because the solids retained on glass fiber filters define the TSS measurement. Samples were analyzed immediately after collection or were preserved until analyzed using accepted preservation methods.[27]

All effluent data were compared after plotting values on log-normal probability papers. Single straight line data fits were determined by calculating 50th and 90th percentile values. The 50th percentile values equaled the antilog of the mean of the log values of data sets. The 90th percentile values were calculated assuming a single-tailed log-normal data distribution

$$\ln N_{90} = \ln N_{50} + 1.282 \ln S_d$$

where

S_d is the standard deviation.

Engineering judgment was used to determine which data sets being compared appeared different and required additional statistical analyses to confirm significance of median differences. Median data values were compared to determine if they were from the same population using a paired t-test[28] assuming a log-normal distribution as follows:

$$\text{compute } t = \frac{\overline{d}}{\sqrt{\dfrac{\Sigma d^2 - (\Sigma d)^2/n}{n(n-1)}}} = \frac{\overline{d}}{\sqrt{S_d{}^2/n}}$$

$$\overline{d} = \text{mean of differences} = \sum_1^n d_i/n \text{ where } d_i = \ln x_i - \ln y_i$$

for $i = 1,2,3,.,.n$ of n data pairs

S_d = standard deviation of d_i.

The test hypothesis is that data are from the same population, therefore, their true medians are equal. This hypothesis is rejected if the calculated t-value exceeds the tabled two-tailed t-value for n-1 degrees of freedom for the selected (90 percent) confidence level.

RESULTS

1. Part I - Pretreatment

The blended refinery wastewater contained excessive amounts of colloids and TSS coated with oil, complicating pretreatment. The DAF unit chemical dosages were relatively high at 40 mg/l filter alum ($Al_2(SO_4)_3 \cdot 14.3$

H_2O) and 20-40 mg/l Dearborn 431 cationic polymer. Chemical dosages were initially optimized using zeta potential titrations in conjunction with jar tests; however, only jar tests were continued since zeta potential calculations became tedious and inconsistent due to the high wastewater specific conductivity (usually 4000-8000 micromhos/cm). This salinity was primarily due to the brackish intake waters to the refinery and may have impeded chemical coagulation at lower chemical dosages as reported by Grutsch and Mallatt.[8]

The superiority of the optimized DAF unit (operating at 1.5 gpm/sq ft) as a pretreatment system over simple sand filtration is clearly evident in the three weeks of run data represented in Figure 2.

DAF unit effluent 50th percentile TOC (158 mg/l) was 55 percent less than the 50th percentile TOC (352 mg/l) in the equalization basin influent to the DAF unit, while the sand filter gave only a 18-percent reduction. Since, at best, only a 31-percent TOC reduction could be achieved by vacuum filtration of equalization basin samples with glass fiber filters (which define TSS), the true effectiveness (55 percent reduction) of colloid and oil coagulation and removal in the chemically assisted DAF unit can be seen. The DAF unit effluent contained essentially only soluble organic contaminants.

The continuous dual-media filter (operating at 4.6 gpm/sq ft) could only manage a TOC reduction of about one-third of the DAF unit. There was no indication that a shorter run time would improve the filter effluent significantly. It appeared that due to the nature of the solids, chemical addition to the filter feed would have been required for an improved system. The purpose of the filter, however, was to produce a biological reactor feed with characteristics comparable to DAF treatment without chemicals. It was observed, on occasions, that DAF pretreatment was very poor when chemical feed pumps failed.

Figure 2 illustrates COD removal by both pretreatment systems employed and again demonstrates the effectiveness of optimized DAF treatment. As in subsequent graphs, the data points are not shown to avoid congestion of data.

Fiftieth percentile oil and grease values during Part I of this study were 101, 70, and 16 mg/l for the equalization basin, filter effluent and DAF unit effluent, respectively. The equalization basin 50th percentile TSS level of 78.0 mg/l was reduced to 57.5 mg/l by the filter and to 19.0 mg/l by the DAF unit. A portion of the TSS in the DAF unit effluent was due to biological growth rather than influent solids. It is possible that part of the organics reduction through the DAF unit was the result of biological activity which could also occur in full-scale systems.

2. Part I - Activated Sludge Performance

TOC and COD (filtered) effluent variability plots for pilot-scale 18-hr retention ASU's are compared in Figure 3. These results are from the initial 3-week data run.

Control ASU F produced a better effluent than control ASU A, both operating at equal 0.3 lb TOC/lb MLVSS-day (F/M) loadings. MLVSS levels in ASU A averaged 1,148 mg/l, about twice that of ASU F due to a twofold increase in feed TOC. Considering both TOC and COD removal, ASU B, C, E, and F did not show any significant overall difference in performance. Fiftieth percentile TOC values ranged from 53-58 mg/l while COD values were 97-116 mg/l as shown in Figure 3. Sludge age was not a controlling performance variable as ASU B (50-day SA) and ASU F (about 10-day SA) differed greatly in solids retention time with average MLSS levels of 1,621 mg/l and 816 mg/l, respectively. Chemically assisted pretreatment for removal of colloids and oil had the most significant effect on organics removal. The high-surface-area powdered carbon (designated PC-H) significantly enhanced organic removal in ASU D, with a 50-day SA and a 500-mg/l PC-H operating level. Enhancement was not evident in ASU C containing the conventional-surface-area powdered activated carbon (designated PC-C). Powdered carbon addition increased the average ASU C MLSS level to 1,885 mg/l with ASU D averaging 1,976 mg/l.

Since a marginal enhancement occurred with the addition of PC-H at a 500-mg/l level, the scope of this investigation was expanded to evaluate powdered activated carbon addition at a 1000-mg/l level and only PC-H at approximately 2500 mg/l. This would give a greater overview of the enhancement capabilities of powdered carbon, especially the highly active PC-H. ASU E was taken out of service since it was only succeeding in lysing biological cells as a second stage following ASU B. The reactor was placed in parallel with other units being fed by the DAF unit and redesignated ASU G. The SA was maintained at 50 days and PC-H was built up to a reactor level of about 2500 mg/l for Part II of this study.

3. Part I - Granular Carbon Adsorption

Granular carbon Series A, treating ASU A effluent, exhausted two 130-gram carbon beds during 17 days of a 3.4-gpm/sq ft hydraulic loading in Part I. A 20-mg/l soluble (filtered) TOC and a 44-mg/l soluble COD effluent (50th percentile, Figure 4) was produced with 0.10 and 0.09-g TOC/g carbon accumulative loadings at exhaustion. Carbon Series F, treating ASU F effluent, reduced the 50th percentile effluent soluble TOC and COD to 23 mg/l and 40 mg/l, respectively. Because of the relatively few data points used to establish Figure 4, there is little significance in the difference between carbon series A and F 50th percentile values. A single carbon bed was exhausted to a 0.12-g TOC/g carbon loading. TOC loadings of carbon columns in Series A were comparable to an average of 0.11 g TOC/g carbon reported for the granular carbon during the four previous exhaustions prior to each regeneration.

Granular carbon effluents were of substantially better quality than all biological unit effluents. The 50th percentile soluble TOC and COD reductions in carbon Series A were 44 mg/l and 84 mg/l, respectively, whereas carbon Series F accounted for a 50th percentile 35-mg/l soluble TOC and 65-mg/l soluble COD reduction.

4. Part II - Pretreatment

Pretreatment by filtration and chemically assisted DAF treatment continued as in Part I of this study. Again, using dosages of 40-mg/l filter alum and 20-40 mg/l Dearborn 431, optimized DAF pretreatment reduced the equalization basin TOC and COD by more than 50 percent as shown in Figure 5. Filtration could only remove gross quantities of oil and solids without preliminary chemical coagulation. Although equalization basin, filter, and DAF unit effluent 50th percentile TOC and COD concentrations were approximately equal to those experienced in Part I of this study, there existed a greater degree of variability in Part II. A contributing variability factor was the rainfall dilution of refinery wastewater streams as an average of 0.21 in./day of rain fell during Part II compared with 0.06 in./day during Part I.

5. Part II - Activated Sludge Performance

The effluent quality for Part II, basis filtered TOC and COD, is given in effluent frequency distributions, Figure 6, for the six-week run period. Control ASU A (F/M = 0.3), without optimized pretreatment, continued producing the most inferior effluent and experienced three upsets due to the development of a filamentous bulking sludge. The unit was restarted on each upset occasion with new seed and allowed to acclimate for a few days before effluent data were used for comparison with parallel systems. ASU B, C, and F, as in Part I, produced nearly equivalent effluents in terms of filtered TOC and COD with neither high SA (50 days) nor 1000 mg/l PC-C enhancing biological treatment. PC-H added to ASU D and G at levels of 1000 and 2500 mg/l, respectively, reduced TOC and COD substantially. Compared with high SA control ASU B, 50th percentile TOC was reduced an additional 10 mg/l and 22 mg/l in reactors D and G, respectively. COD 50th percentile reductions below reactor B were 22 mg/l for ASU D (1000 mg/l PC-H) and 39 mg/l for ASU G (2500 mg/l PC-H). The ASU G run time was abbreviated, however, due to the time required for acclimation at the higher PC-H level. As in Part I of this study, it was observed that as powdered carbon levels were suddenly increased in ASU C, D, and G, performance was exceptionally good for a short period of time.

Phenols feed concentrations were higher in Part II of this investigation as 90th percentile values reached 18 mg/l, compared with 8.5 mg/l in Part I. ASU D (see Table 1) and G, containing PC-H, provided the best phenols removal with 50th percentile phenols levels of 0.05 mg/l and 0.04 mg/l, respectively. This was slightly lower than the high SA control ASU B (0.06 mg/l) and low SA control ASU F (0.07 mg/l). Although the lack of optimized pretreatment produced higher 50th percentile phenols levels (0.11 mg/l) in ASU A, even poorer reductions were experienced with ASU C as in Part I. Similar results were obtained in Part I. An occasional high phenols value was measured in the effluents of ASU D and G but not with the consistency or magnitude of ASU C.

Effluent oil and grease values, included in Table 1, illustrate the significance of removing most of the oil and grease before biological treatment. The 18 mg/l 50th percentile oil and grease effluent level of ASU A greatly exceeded the concentration of 5 mg/l, or less, discharged from reactors receiving optimized pretreatment. The addition of PC-H to ASU D and G gave slight oil and grease improvement with SA alone not being an enhancement factor.

Effluent TSS levels were high in ASU A at a 50th percentile level of 86 mg/l. TSS increased to more than 150 mg/l when filamentous sludge bulking occurred. However, ASU's with DAF pretreatment produced a more settleable sludge. The high SA control ASU B had a significantly higher effluent TSS level than the lower SA control ASU F, but the high SA could be maintained. ASU C and D experienced effluent TSS levels less than control ASU B despite higher reactor solids due to powdered carbon. No effluent TSS increase was observed in ASU G due to the higher (2500 mg/l) PC-H level.

Ammonia nitrogen removal in system A was less than the 80 percent achieved in the systems with optimized pretreatment. The organic loading was higher and the sludge age was less than in other systems. The factors controlling the degree of nitrogen removal were not investigated. Nitrification during Part II was not as complete as that obtained in Part I.

Sludge Characteristics and production rates are summarized in Table 2 for all ASU's. As expected, ASU A had the highest measured oxygen uptake averaging 0.16 mg oxygen/l-min due to a higher influent organic concentration. Oxygen consumption averaged 0.10-0.12 mg oxygen/l-min in other ASU mixed liquors, but a relationship of increased oxygen demand and enhanced biological treatment did not exist. The sludge volume index (SVI), a measure of sludge compactability, significantly improved with SA and powdered carbon addition. Sludge settling velocities were exceptionally high with the worst rate (ASU A) being 0.17 ft/min corresponding to a 1830-gpd/sq ft clarifier rise rate. Other mixed liquors settled with zone settling velocities of 0.34-0.39 ft/min. The average MLSS concentration of 745 mg/l in ASU F was too low for zone settling to occur. One of the most surprising results of powdered carbon addition was that less biomass was produced than in control systems. ASU G produced an average of 0.08 lb biomass/lb COD removed compared with control rates of 0.22 for ASU A and 0.19 for ASU F. PC-H was more effective than PC-C at reducing biomass production rates at the same SA. The total sludge production of activated sludge powdered carbon systems was not much higher than controls, due to lower biological sludge production rates.

Powdered carbon inventories and makeup requirements for ASU's are summarized in Table 3 for Parts I and II of this study. PC-C losses were slightly higher than PC-H but still reasonably close to 2 percent per day. Since biological sludge was wasted at a rate of 2 percent per day in high SA reactors, it is a fairly good assumption that powdered carbon lost in effluents was in the same proportion to biological sludge as in the mixed liquor. Thus both biological and powdered carbon SA may be assumed to be equal for simplification of powdered carbon daily makeup requirements. The powdered carbons must be wetted to prevent loss of floating carbon in the clarifier. This was accomplished by boiling the carbon slurry in this study. Vacuum degassing could also be used.

Another observation made during Part II was that activated sludge-powdered carbon systems significantly reduced aeration basin foaming compared with control systems. Foaming in ASU aeration basins was not a problem but did occur occasionally.

6. Part II - Granular Carbon Adsorption

A single granular carbon bed was exhausted from carbon Series A with an accumulative organic loading of 0.15 g TOC/g carbon during Part II. The data include three short runs. The first two carbon beds required backwashing almost daily due to high TSS levels which could not be continuously removed by dual-media filtration. Fiftieth percentile effluent soluble TOC was 30 mg/l (see Figure 7) for a reduction of 38 mg/l from ASU A. ASU A 50th percentile soluble COD was reduced by 84 mg/l to 79 mg/l. Although phenols levels were generally low (50th percentile of 0.04 mg/l) a few very high effluent phenols levels were detected in carbon Series A giving a 90th percentile phenols value of 4.8 mg/l (Table 1). Phenols must have been adsorbed, concentrated, and then eluted in slugs from the carbon beds to achieve such a high level. Effluent oil and grease levels remained low with 50th percentile values less than 3 mg/l.

Carbon Series F exhausted a single carbon bed to an accumulative organic loading of 0.13 g TOC/g carbon while surpassing the performance of carbon Series A. The 50th percentile soluble TOC was significantly lower at 18 mg/l for a 28 mg/l reduction (Figure 7) from ASU F. Fiftieth percentile soluble effluent COD was 64 mg/l for a 44 mg/l reduction. Phenols levels were extremely low at 0.02 mg/l (50th percentile) and no sudden loss of adsorbed phenols was detected during most of the Part II data run (Table 1). Oil and grease effluent levels (50th percentile) were again less than 3 mg/l.

The lower dashed lines in Figure 7 represent the performance of ASU G, the best of the activated sludge-powdered carbon reactors. ASU G produced an effluent superior to carbon Series A and approached the quality of carbon Series F. The powdered carbon enhancement removed about 85 percent of the soluble TOC adsorbed on carbon Series F and about 60 percent of the COD based on 50th percentile effluent values. The 2,500 mg/l PC-H operating level in ASU G significantly reduced effluent color to a level comparable with granular carbon effluent color.

7. Economics

Although unequal in overall performance, a high SA activated sludge-powdered carbon system (ASU G, 72 mg/l COD) approached the level of granular carbon adsorption (carbon Series F, 64 mg/l COD) to within 8 mg/l COD at the 50th percentile point. Both systems would require extensive pretreatment and tertiary suspended solids removal. All other process components being essentially equal, daily carbon usage costs were estimated for theoretical plant flows of 1-5 MM gpd.

The cost of virgin powdered carbon (PC-H or PC-C) was estimated at $0.30/lb and it was assumed that wasted carbon would be thrown away. To calculate the equivalent powdered carbon dosage required for an 18-hr retention ASU it was assumed a 50-day SA would be maintained, giving an average 2 percent powdered carbon makeup. This was the equivalent of a 37.1 mg/l powdered carbon addition rate based on influent flow. A powdered carbon feeder and storage facilities were included in powdered carbon costs using Du Pont economics[16] and applying the 0.6 rule. It was assumed that the powdered carbon feeder could handle a 50 mg/l addition rate.

Regenerated granular carbon adsorption costs were estimated, using Brown and Root, Inc. economics,[29] and converted to 1977 dollars. Daily granular carbon costs were estimated using 17.2 percent of the fixed investment for operating and maintenance cost and 17.7 percent for depreciation. The total daily costs for powdered carbon were estimated using the same percentage allowances.

Daily estimated carbon costs are shown in Figure 8 for theoretical flows of 1-5 MM gpd by scaling up ASU G and carbon Series F carbon requirements. The cost effectiveness of the relatively simple process change of adding powdered activated carbon to the activated sludge process can be clearly seen. Estimated daily cost savings would range from $987/day at 1 MM gpd flow to $2750/day at 5 MM gpd using high-surface-area powdered carbon (PC-H) addition rather than granular carbon adsorption. The incremental cost would be about $14.73 per pound of COD at 1 MM pgd (see Figure 9).

DISCUSSION

1. Increasing Sludge Age (SA)

Contrary to conventional activated sludge design techniques, the increased SA did not result in sludge deflocculation, higher SVI, and high effluent TSS. With the exception of a few days, the high SA control ASU B easily achieved a high SA as a result of good pretreatment as proposed by Grutsch and Mallatt.[10,11] However, no enhanced performance was measured at the high SA nor in the two-stage system with both reactors at a high SA in Part I. Possibly more emphasis should be placed on the benefits of optimized pretreatment than on increased SA as parallel activated sludge systems at about the same SA (F/M = 0.3) were vastly different in performance at contrasting degrees of pretreatment.

Increasing SA gave a reduction in biological solids production as the conventional F/M control ASU F produced 0.19 lb VSS/lb COD removed compared with 0.16 for high SA control ASU B. This sludge production was not quite as significant as it would have been if ASU F had operated at 5-10 days SA where many conventional ASU's operate instead of about 14 days. Any reduction of biological solids production would help lower sludge treatment and disposal costs.

The high effluent 50th percentile ammonia level of ASU A (11.5 mg/l) in Part II was probably the result of upset conditions which resulted from filamentous sludge bulking causing the loss of biomass. The calculated 10-day SA of ASU A was only slightly less than ASU F (14 days) which produced a 50th percentile ammonia level of 2.3 mg/l in Part II. Although increasing SA generally does improve nitrification, no conclusions could be drawn as to its effect in this study. The conventional ASU F had already produced an effluent that was about 90 percent nitrified.

2. Activated Carbon Enhancement Mechanism

A 0.59-g TOC/g carbon loading was calculated in ASU G while operating with a 2500 mg/l PC-H level. This extremely high "apparent" TOC loading, as explained by Flynn,[16] may be the result of continuous adsorption of slowly biodegraded organics which are "biologically regenerated" from the carbon many times over the biological and carbon SA. "Apparent" TOC loadings therefore increase with higher SA, optimizing the use of powdered carbon, until the carbon becomes loaded with completely biorefractory organics. This explanation of an "apparent" loading or enhancement mechanism appears logical; however, oxygen uptake and biological sludge production data presented here negate biological regeneration in this study. ASU G not only had comparable oxygen uptake measurements with control ASU B, but it produced about 50 percent less biological solids. This implies that the actual enhancement may have been predominantly due to adsorption on the high PC-H surface area. Considering that PC-H had approximately five times the surface area of conventional powdered carbons, such as PC-C, the expression of the TOC loading as 0.12 g TOC/500 sq m of surface area would be more reasonable.

DeJohn[19,30] explains that granular carbon columns are sometimes undersized because the designer uses virgin carbon and assumes that regenerated carbon will have the same activity. The thermal regeneration process will enlarge some carbon pores reducing the surface area and decreasing the adsorption of small molecules which are not so strongly adsorbed on larger pores. Assuming that many small molecules require small powdered carbon pores for moderately strong adsorption, PC-H may have been more effective than PC-C because of pore size distribution, provided that the normally biorefractory refinery organics were small molecules.

The mechanism of powdered carbon enhancement of the activaged sludge process was not defined in this study and needs further investigation in Phase II. Target SA's of the activated sludge-powdered carbon systems were 50 days. Ideally, systems should be operated for periods of several SA's to insure that equilibrium conditions have been reached and that the low (2 percent) daily powdered carbon makeup rate will continue to give consistent results.

The selection of the best powdered carbon for a particular activated sludge enhancement is not a simple task since powdered carbons vary in their adsorptivity. Carbon isotherms performed on a refinery wastewater would exhibit a wide variability and require a statistical analysis to select the best powdered carbon. Isotherms would have to be performed on the activated sludge effluent (as in Phase II of this study) to determine enhancement strictly due to adsorption.

The powdered activated carbon (PC-H) utilized with very good enhancement results is not, as of yet, commercially available. Because of the relatively high cost of granular carbon adsorption, other powdered carbons at similar and higher operating levels would probably offer a significant improvement in activated sludge performance and remain more cost effective than granular carbon.

3. Granular Carbon Adsorption

Granular carbon adsorption data indicate that the quality of end-of-pipe refinery wastewater treatment depends on optimization of each treatment step from primary to tertiary treatment. The use of equilibrium or regenerated granular carbon in pilot studies will provide a more realistic data base, recognizing that economics would favor regeneration for many potential users.

The classical approach[31,32,33,34] for handling carbon adsorption data to establish breakthrough curves was virtually useless in this study because it assumes the carbon column influent has a single adsorbate. In the calculation of accumulated TOC loadings at apparent breakthrough of carbon columns there were several instances where organics were eluted in slugs from carbons in both series. At times, phenols were two orders of magnitude higher than normal. This phenomenon is a very real problem and must be considered when establishing stringent effluent discharge guidelines for industry. Even the best available technology, disregarding economics, has its limitations.

SUMMARY

The EPA 1983 guidelines for the petroleum refining industry have assumed that 1977-type technology must be upgraded by the addition of costly systems, such as granular activated carbon adsorption. The results of this API study indicate that, should the EPA adhere to the granular carbon technology originally proposed, it may be possible to achieve this level of treatment technology by the much more cost-effective method of adding powdered activated carbon to the 1977 activated sludge system.

Process modifications including optimized pretreatment and the addition of a high-surface-area powdered activated carbon can be used to produce an effluent which is comparable in quality to that obtained by granular carbon adsorption. Increasing activated sludge age from the conventional mode of operation (about 10 days) to about 50 days did not give a significant system improvement; however, in conjunction with powdered carbon addition, high sludge age allowed higher equilibrium reactor concentrations (2500 mg/l) at low (2 percent) carbon makeup rates. This benefit has been demonstrated with the high-surface-area carbon and it is possible that it can also be obtained with increased levels of conventional powdered carbon. The cost-effectiveness of any powdered carbon will depend on the wastewater characteristics and powdered carbon adsorptivity, which was greater for the high-surface-area carbon (2462 sq m/g) than for the conventional-surface-area carbon (550 sq m/g) investigated here. Even granular carbon adsorption was found to have limitations as slugs of phenols were eluted, on occasion, into the effluent.

ACKNOWLEDGEMENTS

This study was funded in part by the American Petroleum Institute, Divison of Refining, CREC Liquid Waste Subcommittee.

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BIOGRAPHY

Leonard W. Crame

Leonard W. Crame is a Senior Chemical Engineer in the Air and Water Conservation Section of Texaco's Prot Arthur, Texas, Research Laboratories. He has a B.S. degree in Engineering Technology (Chemical) and an M.S. in Thermal and Environmental Engineering from Southern Illinois University at Carbondale. Len has been involved in several refinery wastewater treatment pilot studies and conceptual designs since joining Texaco in 1973. He is a member of the Texas Water Pollution Control Association and has recently authored several papers on wastewater treatment.

DISCUSSION

E. A. Buckley, Lion Oil Co.: What were the levels of alum and polyelectrolyte used in the DAF pretreatment to the system?

Len Crame: In the dissolved air flotation unit we were using, we found by the use of the zeta meter and jar tests that it required 40 milligrams per liter of filter alum, 20 milligrams to 40 milligrams per liter of catonic polymer Dearborn 431. It was not the intent of this study to try to zero in on the best and most economical chemical dosage but mainly to get the soluble feed for the bio units. We found from experience that wide fluctuations in the feed characteristics did not affect these two chemical doses.

Ed Sebesta, Brown & Root: In the slide (Figure 2) comparing effluent and COD concentrations from the various pretreatment systems, were the samples filtered or unfiltered?

Len Crame: They were filtered COD's for our bio effluents and carbon effluents. In Figure 2, I did not identify them, but it is total COD. It does include suspended solids because we were looking for the contribution of solids in this case.

I also would like to make the comment that I do pretty much agree with everyone else's presentations as far as what work has been done with carbon on the enhancement mechanism and we will continue to look at this throughout the second phase of our pilot study. I think that you have to be very careful in using powdered activated carbon. In a short term study I agree with the other gentlemen (Amoco)(DuPont), that when you first put in activated carbon you have to allow time for this matrix to form, which we did. And you don't get the same settling effect as when you initially add carbon. When you allow the system to come to an equilibrium and the bio-mass starts adhering to the powdered carbon, it does greatly improve the sludge settling characteristics, but it takes a little time. I believe that when you initially add powdered carbon your results are going to be very good because you're going to get a tremendous amount of adsorption. We followed this and have seen it. I'm very hesitant about including data right after you start running an enhanced bio-system. You will see a sharp decrease in the effluent organic levels. You have got to wait until an equilibrium is reached.

J. Dewell, Phillips Petroleum Co.: In your cost comparison between enhanced activated sludge and the granular carbon, I wasn't sure if the enhanced activated sludge assumed that the conventional activated sludge was already in place or not. Would these comparisons still be valid on a grass-roots treating system?

Len Crame: We were assuming that activated sludge was already in place and actually we were only comparing the cost of carbon contactors and regeneration equipment against the additional equipment you have to put in to add powdered carbon. We were not including filters. We would believe the filter would have to be a part of both treatment systems and would have no effect on this comparison.

J. Dewell: Do you have any feel for what would be most cost effective on a grass-roots basis, assuming no treatment system at all exists?

Len Crame: I think it is a safe argument that activated sludge is probably the best system for driving the effluent organic levels down for 1977 and 1983 but not necessarily the most cost effective. At this time I do not see any other system that perhaps can be enhanced cost effectively with powdered carbon for 1983.

J. Dewell: I was referring to a situation where one does not have activated sludge at this time and is meeting 1977 standards so one is going to come to 1983 without any activated sludge.

Len Crame: I think this must be determined on an individual basis. As you know when you calculate out guidelines for '77 or '83 you will find that in some cases you are stuck with very tight guidelines for a certain parameter and I don't think it is appropriate to say which type of treatment would be best. We would definitely not put in any powdered-carbon enhanced system until we piloted it and you would be taking a risk if you did. All treatment systems are unique, including activated sludge systems and enhanced biological systems. We think that powdered carbon addition has a lot of merit, but still you should determine it on a case-by-case basis.

F. L. Robertaccio, DuPont: I think that the easiest way to look at it is that the activated sludge system in this case is common to both the powdered-carbon addition and the granular-carbon addition system so the difference in cost here would have added to it the cost of the activated sludge system if you were starting out with a brand new plant. You can use that as a first estimate, but what we have found at the plant I talked about yesterday is that with a grass-roots plant you have additional savings that you can accrue to take full benefit of the system. We talked about having smaller secondary clarifiers, higher upflow rates through the clarifiers, smaller dewatering equipment; and having no secondary solids disposal if you go through regeneration. So our experiences have been that with the grass-roots system you can put in powdered carbon systems with regeneration for the same capital costs and essentially the same operating costs as a conventional secondary wastewater treatment system. If you want further reference on this there was a paper I referred to yesterday that had details of those cost estimates.

J. E. Rucker, API: Please comment on why your COD values were greater than those we looked at earlier this morning from the Argonne work?

Len Crame: The refinery where we were located is a very complex refinery and I am quite sure that the refractory COD that remains is going to differ from plant to plant. We did try to exclude everything from the chemical plant, but I am not surprised really that we have a different refractory COD level and I don't think you can compare the refractory COD's out of these carbon systems from plant to plant and find a great consistency as far as concentration goes.

Jeffrey Chen, Dravo: What would you propose to use to treat the sludge generated from the pretreatment unit? Will the cost associated with the treatment be cost effective when compared to the improvement of the following bio system?

Len Crame: We were assuming that for our best case here that when we were comparing granular carbon with powdered carbon you would have a primary sludge treatment and disposal problem in both cases so that it really doesn't affect our economics here. Sludge disposal is another problem and again it does depend upon the availability of land and other considerations and it is just something totally different; but actually we're comparing the two systems here and assuming that primary sludge is going to be a problem in both cases. You would have to do a cost effectiveness study on the pretreatment and sludge disposal cost vs the benefit obtained from it. But from an operational standpoint, once you get the colloids and oil out it is much easier to operate the activated sludge process, since the oil and solids interfere with flocculation and sludge settling.

Tom McConomy, Calgon Corp.: During the period you were operating the granular carbon columns, was the carbon changed or was the same carbon used during the entire test?

Len Crame: As you will see in the paper we had four carbon columns and we would measure TOC at intermediate points and whenever we found a breakthrough on the first carbon column, we would shift the carbon columns and put a fresh regenerated column on the tail-end of the system. This is why we are confident that the final column effluent is representative of what carbon adsorption can do with the regenerated carbon. We did try to determine how much we had in those columns and we were running about 0.12 to 0.15 pounds TOC per pound of carbon, which I think is fairly typical. But because of the activated sludge enhancement you get with powdered carbon, where I won't necessarily say "biological regeneration" occurs, you are effectively regenerating it somehow by desoprtion, or whatever, within the process and that is what makes it economical.

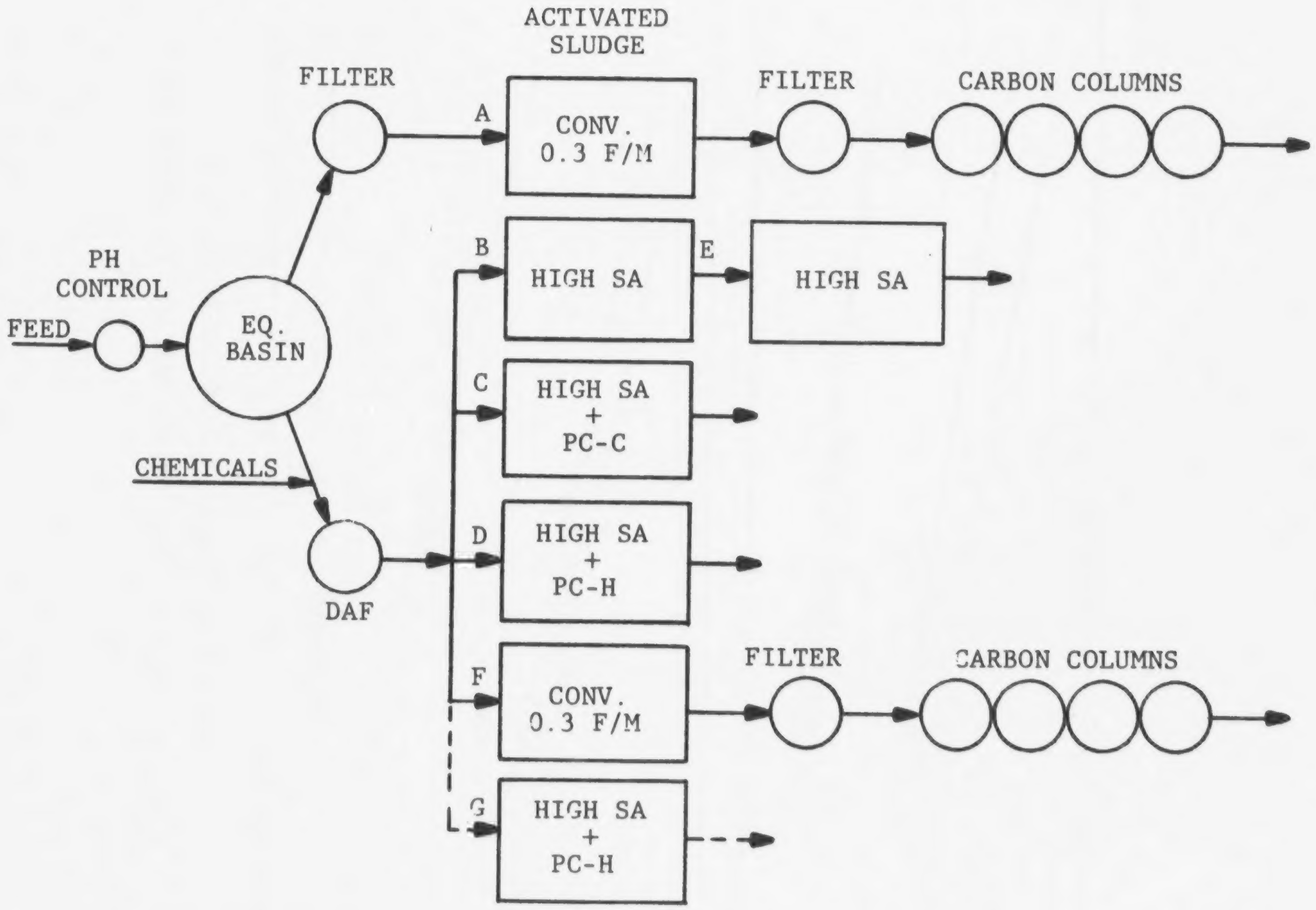

ACTIVATED SLUDGE
FILTER
CARBON COLUMNS
PH CONTROL
FEED
EQ. BASIN
CHEMICALS
DAF
A
CONV. 0.3 F/M
FILTER
B
HIGH SA
E
HIGH SA
C
HIGH SA + PC-C
D
HIGH SA + PC-H
F
CONV. 0.3 F/M
FILTER
CARBON COLUMNS
G
HIGH SA + PC-H

FIGURE 1 - TREATMENT SCHEMES

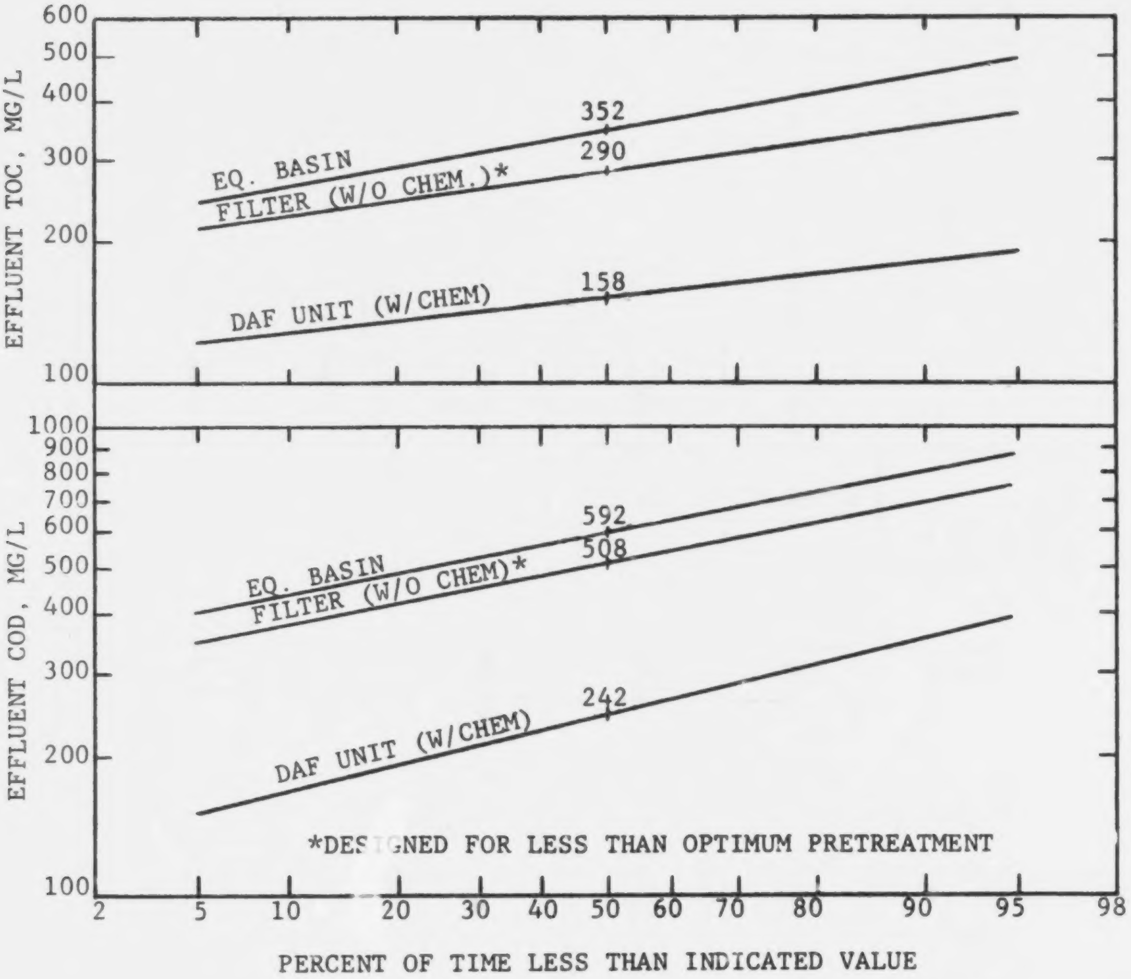
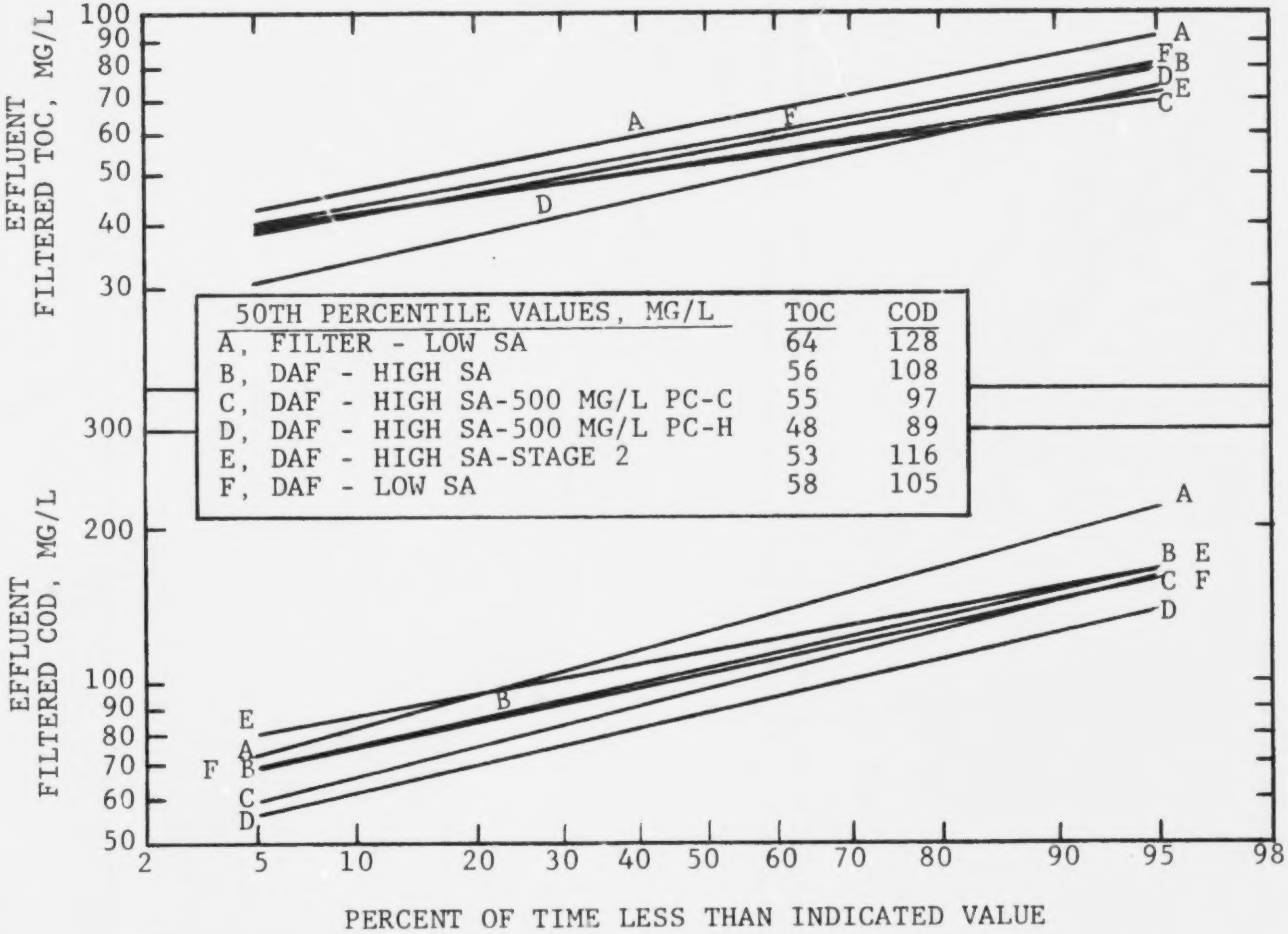


FIGURE 2 - PART I - TOC AND COD REMOVAL BY PRETREATMENT



50TH PERCENTILE VALUES, MG/L	TOC	COD
A, FILTER - LOW SA	64	128
B, DAF - HIGH SA	56	108
C, DAF - HIGH SA-500 MG/L PC-C	55	97
D, DAF - HIGH SA-500 MG/L PC-H	48	89
E, DAF - HIGH SA-STAGE 2	53	116
F, DAF - LOW SA	58	105

FIGURE 3 - PART I - ACTIVATED SLUDGE TOC AND COD DISTRIBUTIONS

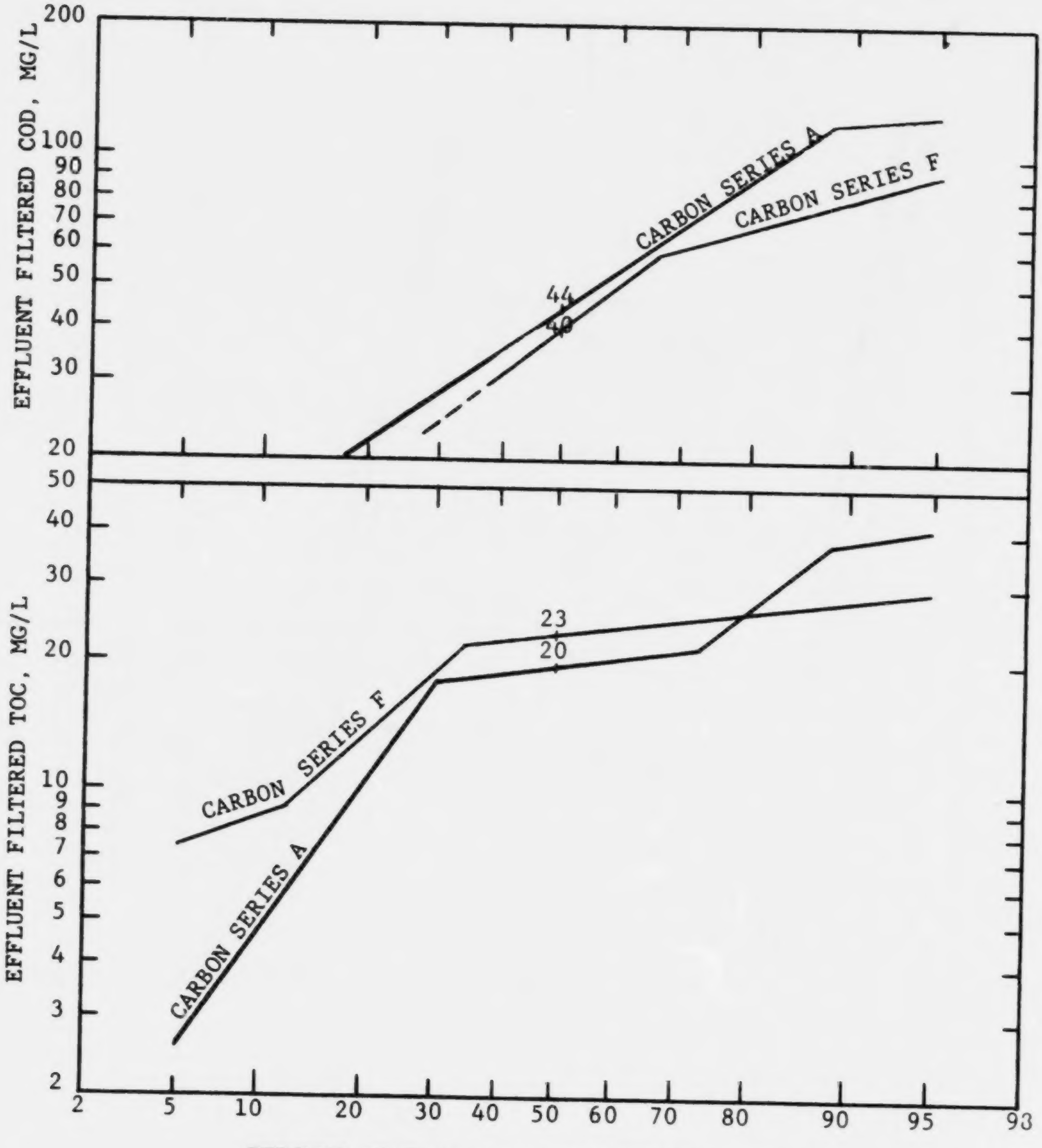


FIGURE 4 - PART I - GRANULAR CARBON COLUMN TOC AND COD DISTRIBUTIONS

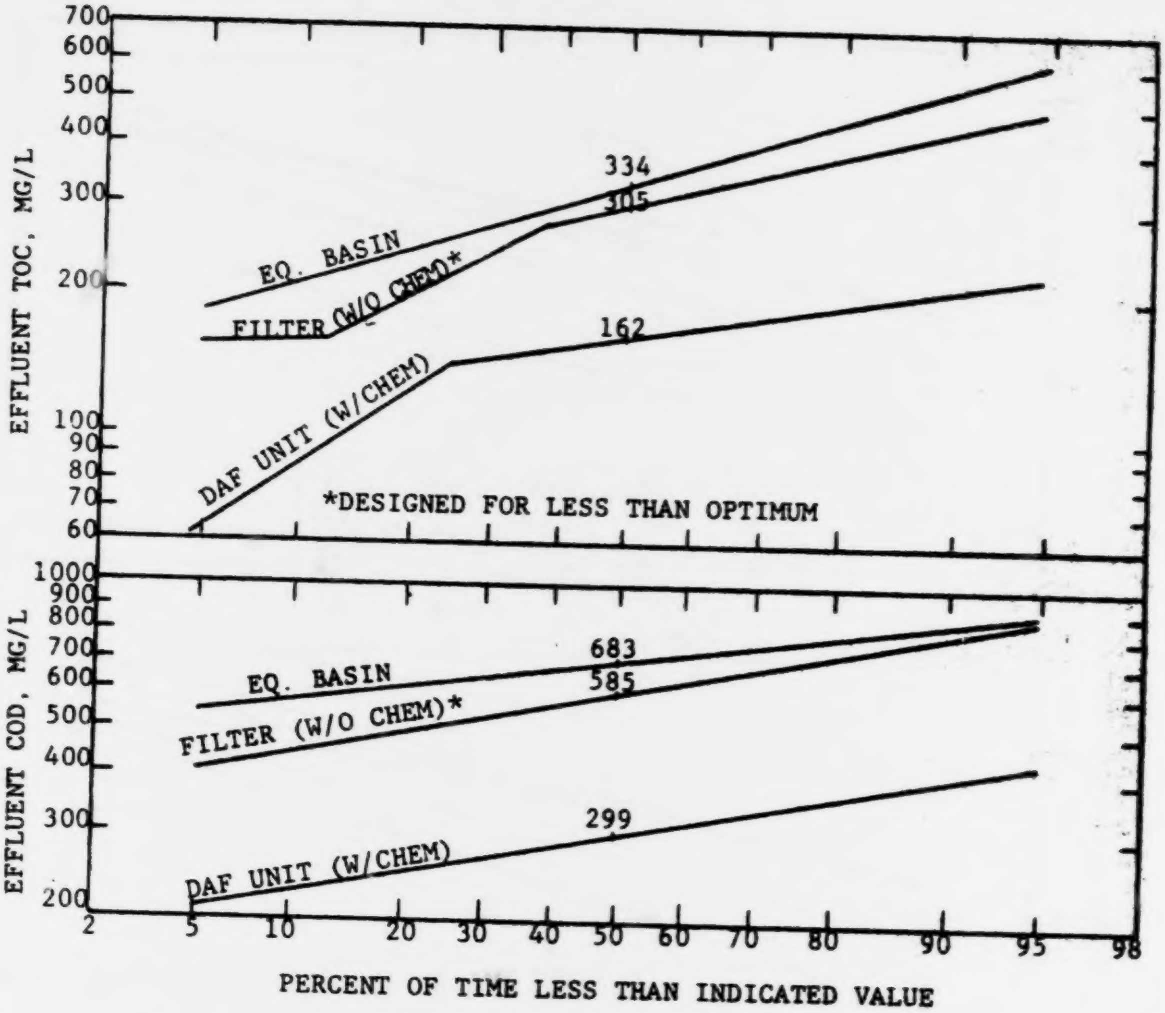
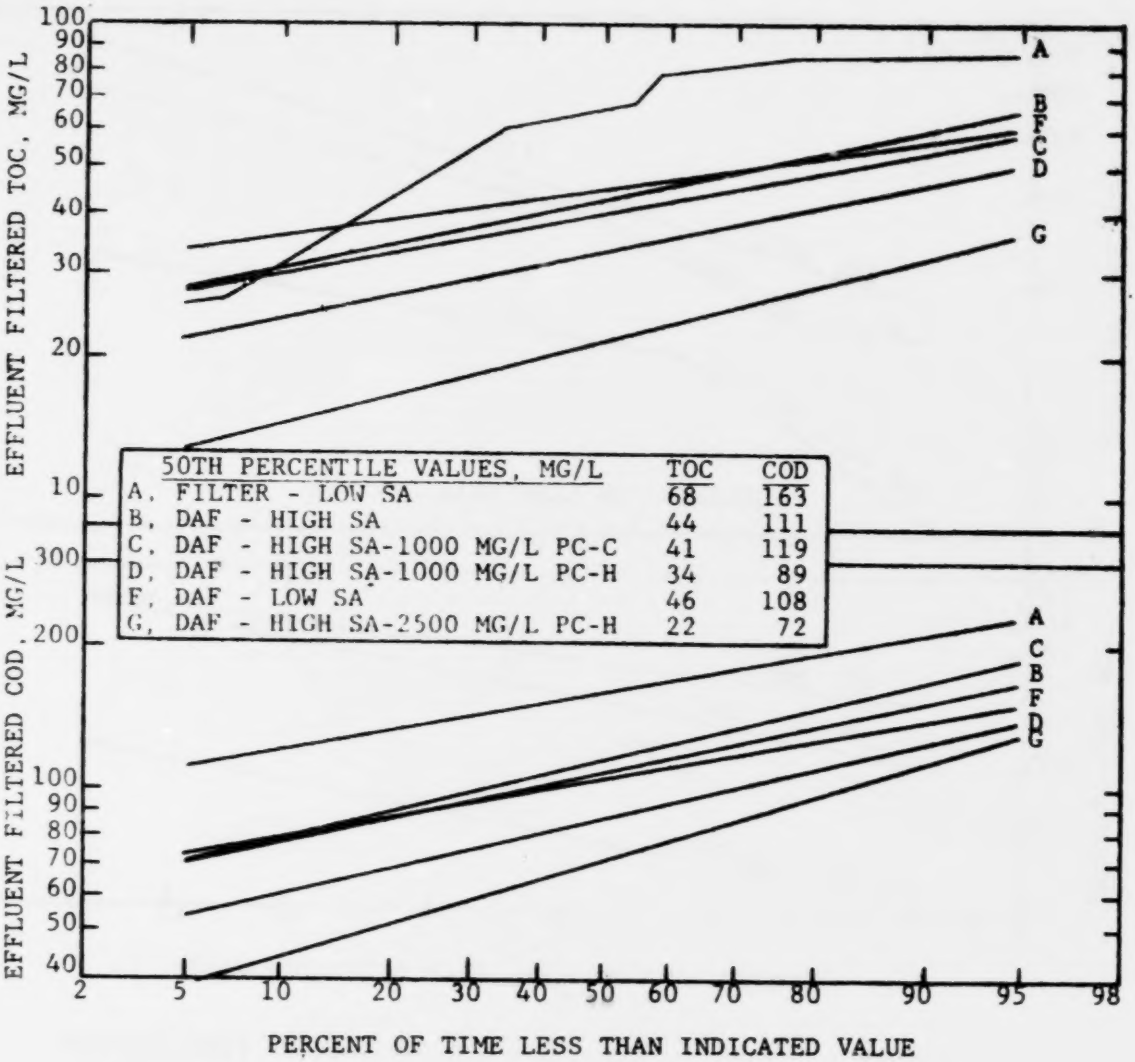


FIGURE 5 - PART II - TOC AND COD REMOVAL BY PRETREATMENT



50TH PERCENTILE VALUES, MG/L	TOC	COD
A, FILTER - LOW SA	68	163
B, DAF - HIGH SA	44	111
C, DAF - HIGH SA-1000 MG/L PC-C	41	119
D, DAF - HIGH SA-1000 MG/L PC-H	34	89
F, DAF - LOW SA	46	108
G, DAF - HIGH SA-2500 MG/L PC-H	22	72

FIGURE 6 - PART II - ACTIVATED SLUDGE TOC AND COD DISTRIBUTIONS

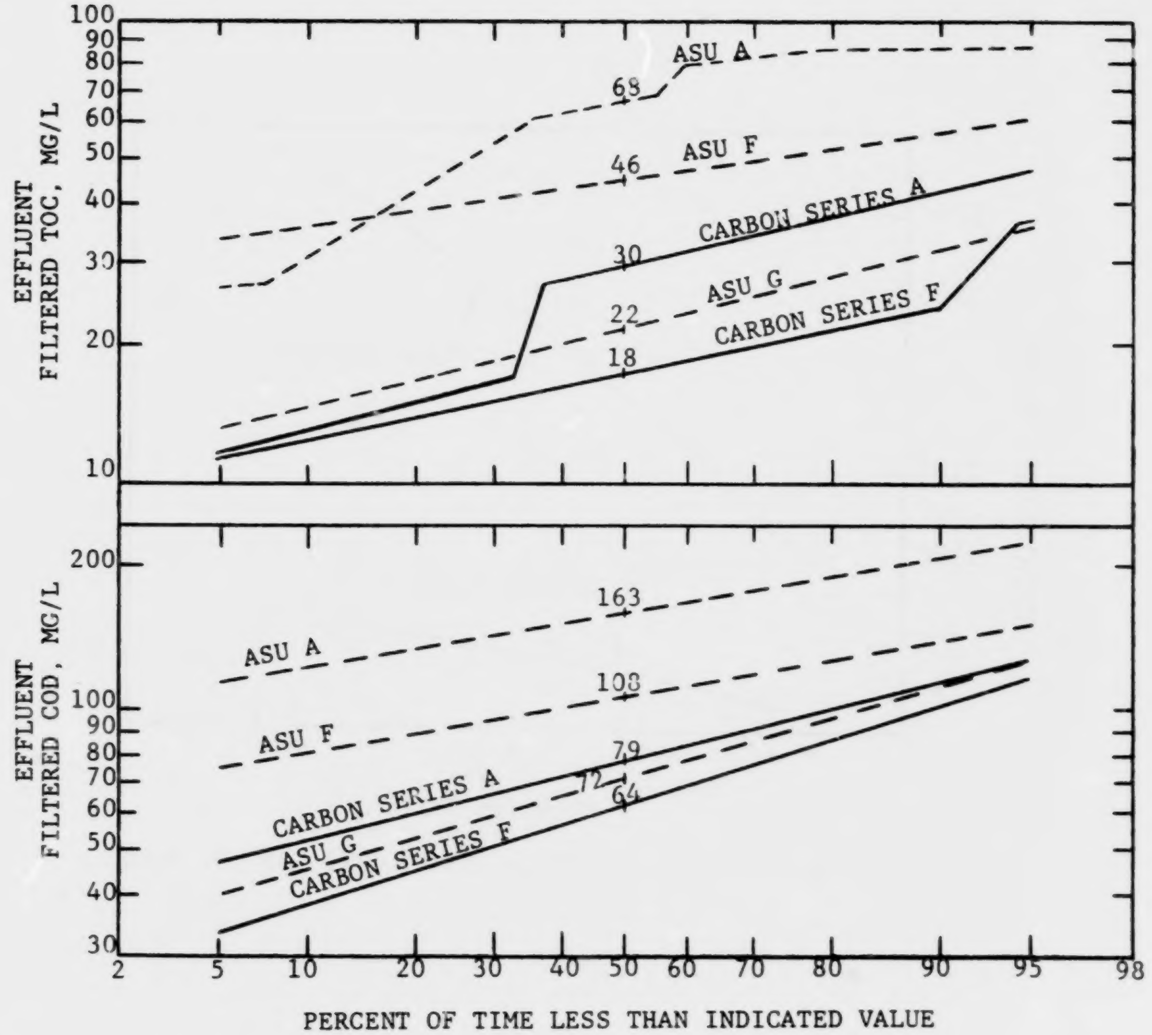


FIGURE 7 - PART II - GRANULAR CARBON TOC AND COD DISTRIBUTIONS

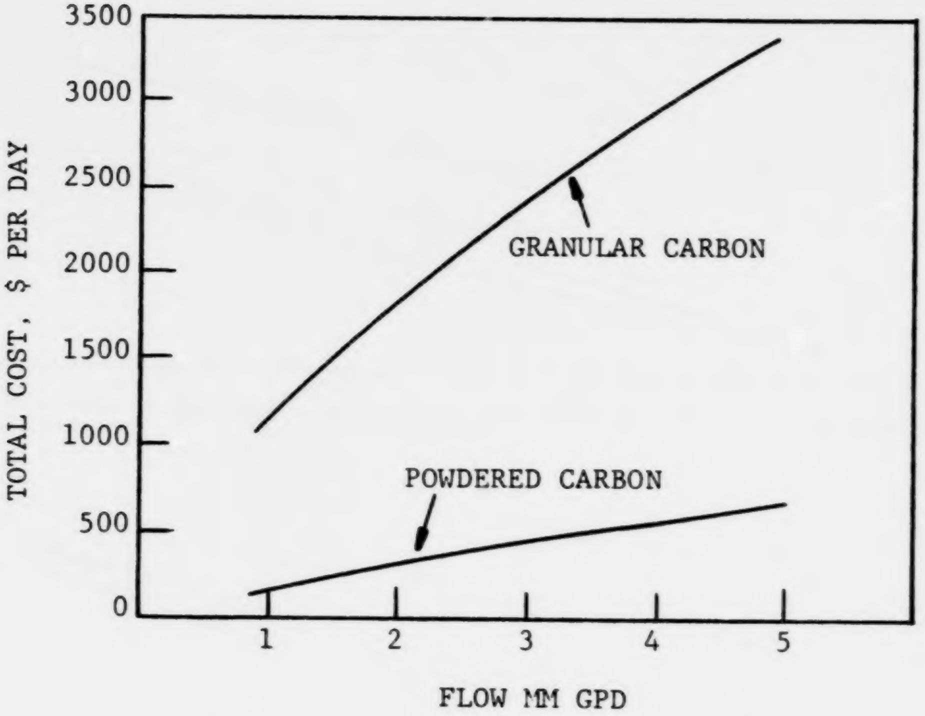


FIGURE 8 - COMPARISON OF ESTIMATED CARBON COSTS

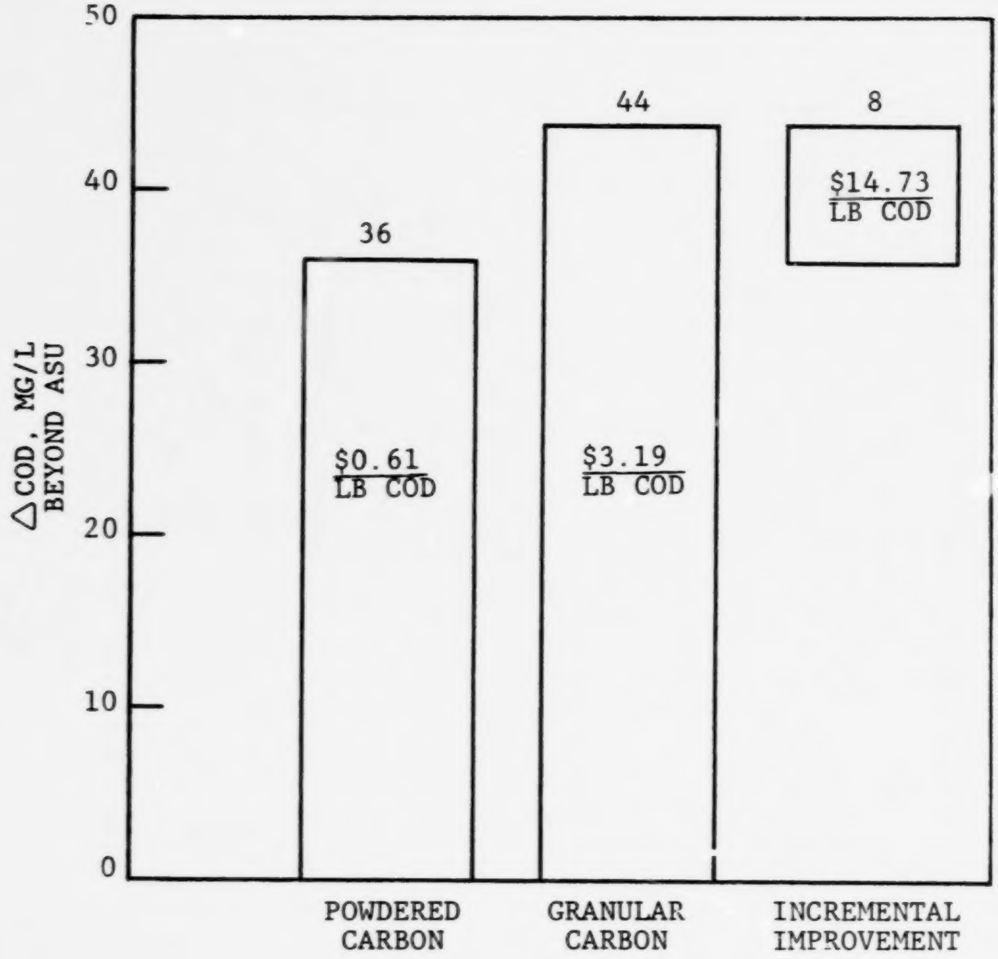


FIGURE 9 - ESTIMATED EFFECTIVE CARBON COST AT 1 MM GPD

TABLE 1- PART II - EFFLUENT SUMMARY

(ALL VALUES MG/L)

EFFLUENT SAMPLE	PHENOLS PERCENTILE		OIL & GREASE PERCENTILE		TSS PERCENTILE		AMMONIA PERCENTILE	
	50TH	90TH	50TH	90TH	50TH	90TH	50TH	90TH
EQ BASIN	7.3	18.0	108	191	64.0	119	20.9	27.2
FILTER	--	--	69	130	34.0	74.0	--	--
DAF UNIT	--	--	14	19	13.0	21.0	--	--
ASU A	0.11	0.16	18	38	86.0	149	11.5	20.0
ASU B	0.06	0.14	5	7	27.5	41.0	3.9	9.2
ASU C	0.15	0.38	3	9	23.0	77.0	3.3	5.4
ASU D	0.05	0.20	< 3	5	18.0	57.0	3.1	4.8
ASU G	0.04	0.13	< 3	3	22.0	44.0	3.1	4.4
ASU F	0.07	0.17	4	7	8.4	28.0	2.3	5.4
CARBON COL. (SERIES A)	0.04	4.8	< 3	6	--	--	--	--
CARBON COL. (SERIES F)	0.02	0.08	< 3	4	--	--	--	--

TABLE 2 - PART II - SLUDGE DATA

AVERAGE VALUE	ACTIVATED SLUDGE UNIT A	 B	 C	 D	 F	 G
NOMINAL LOADING	F/M = 0.3	50-DAY SA	50-DAY SA	50-DAY SA	F/M = 0.3	50-DAY SA
ACTUAL LOADING	F/M = 0.3	39-DAY SA	42-DAY SA	44-DAY SA	F/M = 0.3	56-DAY SA
MLSS, MG/L	1,487	1,892	2,728	2,720	745	4,096
MLVSS, MG/L	1,302	1,562	2,269	2,416	689	3,898
PC, MG/L	0	0	1,000[a]	1,000[b]	0	2,500[b]
% VSS	88	83	83	89	92	95
OXYGEN UPTAKE, LB O_2/LB COD REM MG/L-MIN	0.40 0.16	0.68 0.12	0.71 0.12	0.49 0.11	0.61 0.11	0.47 0.10
SVI, ML/G	95	64	41	43	91	30
SETTLING VELOCITY, FT/MIN	0.17	0.34	0.38	0.38	N/A[c]	0.39
BIOMASS PRODUCTION RATE[d]	0.22	0.16	0.12	0.11	0.19	0.08
TOTAL PRODUCTION RATE[e]	0.25	0.19	0.17	0.14	0.21	0.09

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[a] CONVENTIONAL-SURFACE-AREA.

[b] HIGH-SURFACE-AREA.

[c] DISCRETE SETTLING

[d] LB VSS/LB COD REMOVED.

[e] LB TSS/LB COD REMOVED (INCLUDES CARBON)

TABLE 3 - POWDERED CARBON (PC) REQUIREMENTS

ASU-PART	PC LEVEL (MG/L)	PC TYPE	PC INVENTORY (G)	AVG PC LOSS (G/DAY)	PC MAKEUP (%)
C-I	500	PC-C	28.4	0.68	2.4
D-I	500	PC-H	28.4	0.56	2.0
C-II	1,000	PC-C	56.7	1.50	2.6
D-II	1,000	PC-H	56.7	1.12	2.0
G-II	2,500	PC-H	141.9	2.21	1.6

"PILOT PLANT ACTIVATED CARBON TREATMENT OF PETROLEUM REFINERY WASTEWATER"

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INTRODUCTION

One of the first documented uses of carbon for environmental control was in 1793 when a physician used charcoal to remove the odor associated with gangrene. About sixty years later a scientist by the name of Stenhouse recommended the use of charcoal to remove the odors from sewers. Potable water was "purified" by carbon in 1862.[1] Moonshiners in the hills of Tennessee were using charcoal, not to mellow their product, but to remove "hog track" odors.

Since the mid-1960's, there has been an increasing effort to utilize activated carbon as a secondary or tertiary treatment system to treat wastewater. Two of the most successful uses of activated carbon were demonstrated at Lake Tahoe and in Pomona, California, to treat domestic municipal wastewaters. It is, of course, a natural progression to treat industrial wastewaters with systems that appear successful in treating municipal wastewaters.

The first domestic petroleum refinery to use activated carbon treatment was the Atlantic Richfield Refinery in Carson, California. The system was designed for intermittent use to treat rainfall runoff and process wastewater during storm periods. The second application was designed for the BP Refinery, Marcus Hook, Pennsylvania, to treat process wastewaters. Unlike the Arco system, the BP system was designed to operate in a continuous mode. Neither system relied on biological treatment preceding the activated carbon system.

During the late 1960's, activated carbon treatment of industrial wastewater was gaining momentum as the treatment system of the future. Statements such as "organic removal" or "removal of dissolved organics from wastewater has been demonstrated" and "activated carbon treatment systems will remove dissolved organic contaminants" were prevalent. These innocent gross statements were translated rather rapidly to imply that if you had an organic waste treatment problem, it could be solved with granular activated carbon.

With the complete cooperation of Kerr-McGee Petroleum Refinery, Wynnewood, Oklahoma, a study program was devised to investigate the adsorptive capacity of activated carbon.

ISOTHERM STUDIES

Adsorption isotherms are used to indicate the effectiveness of an activated carbon for a specific wastewater under controlled conditions. When the isotherm is to be used as a predictive tool, the wastewater should be as representative as possible, pH and temperature adjustments should not be made, and sample collections need to be made in glass containers.

CARBON EVALUATION

Eleven commercially available carbons were evaluated for this petroleum refinery's wastewater. It is necessary to point out that adsorption varies with the carbon being evaluated and the water sample. The data presented is based on specific activated carbon for one petroleum refinery. Comparable results may or may not be achieved using the same carbon at another refinery.

The controlled conditions used for comparison purposes of the eleven carbons are shown in Table 1. Both pulverized and granular modes were evaluated.

The waste sample to be evaluated was collected from the API separator discharge, settled for four hours, and the candidate water was drawn from the middle of the vessel. The adsorption capacity of one gram sample of the candidate carbons, both pulverized and granular, is shown in Table 2.

Graphically expressed, the comparison of pulverized and granular adsorption capacities appears in Figure 1.

CONTACT TIME

A major factor relating to adsorption is the amount of time the water to be treated is in contact with the activated carbon. A sample of wastewater from another refinery was obtained for these studies. Pulverized activated carbon (Filtrasorb 400) was weighed to obtain 0.1, 0.5, 1.0, 2.0, and 5.0 grams of sample, and the isotherm procedure was followed for three hours. Samples were obtained at 20, 40, 60, and 180 minutes, filtered, and analyzed for total organic carbon. Table 3 represents the typical results.

ISOTHERM TESTING

Figure 2 shows the results of an isotherm carried out on wastewater from the refinery used in this study and a candidate activated carbon. Obviously, this curve does not follow the typical "Freundlich" isotherm. Instead of the usual straight line, a curve resulted. At the lower end of the curve the amount of carbon added to the wastewater is increased but the concentration of TOC does not decrease as much as would be expected. In fact, the concentration of TOC changes only very slightly at high carbon dosage. Refinery wastewater is composed of a rather complex mixture of materials. Some of these materials are readily adsorbable while others are not. The initial amount of carbon picks up the easily adsorbed materials and leaves behind the others. Therefore, increasing the carbon dosage does not reduce the concentration of TOC to the same degree. In fact, there is a possibility that this wastewater contains non-adsorbable components that cannot be removed by carbon treatment.

From the "isotherm," the adsorptive capacity of the carbon, tested with this specific wastewater, projects to approximately 0.1 lb of TOC per lb of carbon. This was considered to be a reasonable value and indicated that further investigation of activated carbon treatment was justified.

Results from isotherm tests are considered to be valuable only from an initial screening standpoint. Their results are generally not sufficient for predicting results of full-scale granular activated carbon treatment. For a better evaluation of activated carbon treatment, continuous column pilot plant investigation at the waste stream site yields much more reliable results.

ANTHRAFILT FILTRATION

When treating oily wastes by activated carbon, it appears that a pretreatment system is needed to assist in the removal of insoluble oils and suspended matter. An anthrafilt downflow filter system was evaluated for effectiveness, again using filtrable TOC as the prime parameter. The glass column used for this exercise was five feet in length and 1.5 inches in diameter. A diagram of the system is shown in Figure 3. Total organic carbon results obtained at these time intervals are shown in Table 4.

This particular study lasted 2.5 hours before a pressure drop was noted. The charge water contained an appreciable quantity of oil, and the oil percolated into the anthrafilt layer during the study period. When the column was backwashed with distilled water, the percolated oil was easily removed from the anthrafilt, leaving an apparently clean bed.

MINI-COLUMN STUDY

A downflow mini-column system was designed using stock one inch ID glass tubing that was six feet in length. The system was designed with an electronic sampler to composite hourly samples. A diagram of this system is shown in Figure 4.

The primary study involved dividing the six columns into two sets of three columns each to evaluate comparison of treatment effectiveness. Each column was packed with 1,000 cc of Filtrasorb 400 using potable water was the wetting liquid. The flow rate was set at 400 ml/minute and a column pressure of 6-7 psig was used. Total organic carbon was the primary parameter used for treatment effectiveness. Analytical results of the primary study are recorded in Table 5.

Comparing each column for removal efficiency, using the anthrafilt effluent TOC as the base, the percentages obtained are shown in Table 6. Columns 1 and 2 compare very well for the five-day averages, although they do exhibit considerable daily variances. Columns A-3 and B-3 are not agreeable, and no reason for this deviation is projected.

A second study was conducted by connecting five columns in an upflow mode. Each column contained 1,000 cc of Filtrasorb 400 packed in the same manner as the previous study. TOC results of this study are shown in Table 7.

Percentage reductions of each column based on the anthrafilt effluent are shown in Table 8. The average column trend indicates there is an increase of treatment effectiveness with each succeeding column, as one would expect.

PETROLEUM REFINERY DATA

Listed in Table 9 is the pertinent information needed to characterize the refinery where the study was conducted. This refinery was a 30,000 barrel, Class "B" refinery (using the API classification system); processes included fluid cat cracking, HF alkylation, catalytic reforming, and asphalt production.

The existing refinery eastewater treatment system is shown in Figure 5. Wastewater from the refinery includes cooling tower blowdown, boiler blowdown, oily process water, stripper effluent, and contaminated runoff. These wastes flow to an API separator for oil removal. The effluent from the separator is treated in a "Pasveer Ditch" activated sludge treatment system. The biologically treated effluent then flows through a series of holding ponds and the effluent from the final pond is discharged to a small stream.

Two complete pilot plants were installed and operated simultaneously, one on the refinery's API separator effluent (secondary) and the other on the clarifier effluent from the biological treatment system (tertiary).

ACTIVATED CARBON TREATMENT PILOT PLANT

Figure 6 contains a flow diagram of the pilot activated carbon treatment systems. The wastewater to be treated first flows through a dual-media filter constructed of 4-inch PVC pipe. This filter consisted of an 18-inch layer of sand over pea gravel, topped with a 6-inch layer of anthrafilt.

Dual-media filtration pretreatment was chosen because of its reliability and effectiveness, and because it does not require the use of iron or aluminum salts as coagulants. This latter point is particularly important insofar as regeneration of activated carbon is concerned, since aluminum salts during regeneration can remain on the surface of the carbon at high temperatures. These salts can become permanently attached to the surface. Thus, the effective surface area of the carbon is reduced and its adsorption capacity is seriously reduced. Iron salts present a similar problem. In addition, these salts can catalyze oxidation reactions of the carbon and the gases in the regenerator. Thus, the structure of the carbon becomes permanently damaged.

After pretreatment, the wastewater entered a "Calgon" activated carbon pilot plant. This plant was set up so that the wastewater flowed down three of the 5-inch ID columns. The first column contained an 18-inch layer of granular activated carbon while the remaining columns had a 36-inch layer of carbon.

The flow rate through each pilot plant was adjusted to 1/4 gpm. During the operation of the pilot plant, samples of the API separator effluent, biological treatment effluent, and both pilot plants' effluents were taken every two hours. These samples were composited and preserved according to recommended EPA methods. Twenty-four hour composite samples were analyzed daily for a spectrum of water pollution control parameters using EPA analytical methodology and analytical quality control techniques.

The dual-media filter and carbon columns were backwashed whenever the pressure in the first column exceeded 20 psi. The pilot plants were operated over a 10-day period, at the end of which time the first columns in both plants were near exhaustion.

Figure 7 shows the BOD_5 daily composite analysis for the API separator effluent before and after treatment by the various schemes studied. Activated carbon treatment was not able to achieve the same level of BOD_5 reduction as bio-treatment. In fact, bio-treatment did a considerably better job. However, carbon treatment following bio-treatment did show further reductions in BOD.

Figure 8 shows the COD daily composite results for the same wastewater streams. Apparently, both bio-treatment and carbon treatment effect about the same COD reductions. Carbon treatment following bio-treatment yielded the best reduction of COD.

The TOC results for the daily composites are shown in Figure 9. Unlike the BOD_5 and COD results, the TOC indicates increased removal can be obtained by the API-carbon combination over the bio-treatment system alone. There is an erratic behavior pattern which indicates unadsorbable organics passing through the carbon columns.

From the BOD_5 and COD plots, it may be concluded that for secondary treatment alone, on the wastewater studied, the biological treatment system is preferable because it gives the greatest BOD_5 reduction and gives COD reduction equivalent to carbon treatment. The best levels of reduction were obtained with biological treatment followed by carbon adsorption.

Table 10 gives the results of other parameters evaluated in this study. As would be expected, both biological and activated carbon treatments are able to produce significant reduction in the organic parameters, such as BOD, COD, TOC, oil and grease, and phenols. It should be noted that carbon has a particular affinity for the removal of phenols. The color and turbidity are also improved. Cyanides and ammonia, for all practical purposes, were not removed by either of these treatments.

Sulfides are a peculiar problem for activated carbon treatment. Apparently, the sulfide content increases as it goes through the carbon system. This is probably due to biological activity occurring at the surface of the carbon. The sulfur containing compounds which are adsorbed upon the carbon are reduced anaerobically to H_2S giving rise to the increase in sulfide content. Bio-treatment, on the other hand, decreases the sulfide content very significantly.

One of the least expected removals by activated carbon was observed for the metals --chromium, copper, iron, and zinc. These metals are significantly reduced by the carbon. Whether these removals are due to adsorption, filtration, or other phenomena has not been evaluated. However, it must be kept in mind that these removals were accomplished with virgin carbon. The effect of some of these metals upon carbon regeneration has not been determined. Also, whether regenerated carbon can remove equivalent amounts of metals has not been established.

As mentioned previously, the isotherm study indicated that the carbon could adsorb 0.1 lb TOC/lb of carbon. The columns on the API separator effluent indicated a capacity of 0.31 lb TOC/lb of carbon, as shown in Table 11. The most probable explanation for the difference in the capacity as determined in the isotherm test and the pilot plant study is biological activity in the columns.

In the case of the API separator effluent carbon column, this biological activity manifested itself by the anaerobic production of H_2S. While the increased capacity is a desirable situation, the production of sulfides is not. Although anaerobic activity was not apparent in the clarifier effluent columns, it was observed that algae started growing in the carbon beds. In fact, it was necessary to cover the columns to prevent sunlight from making this growth possible.

Because of the considerable cost of granular activated carbon, regeneration of the spent carbon is essential if the cost of treatment is to be kept at a moderate level. Samples of spent carbon were taken from the first column of each pilot plant and sent to Calgon Corporation for regeneration studies. Calgon regenerated these two carbons using their standard evaluation techniques in a muffle furnace at 1750° F and with a normal air, flue gas, and steam atmosphere.

As shown in Table 12, both carbon samples were regenerated to a good activity as indicated by the iodine numbers obtained. The regenerated clarifier carbon appeared to have a little better activity than the API separator carbon. In general, the iodine number can be related to the surface area of pores larger than 10 Å in diameter. The molasses number, likewise, is related to the surface of pores larger than about 30 Å. As can be observed in Table 15, there is an increase in the molasses number with a slight decrease in iodine number. This indicates a shift in pore size distribution. Apparently, the smaller pores are being destroyed while larger pores are being created. Final clarifier carbon appeared to have less destruction of the pore matrix than did the API separator carbon.

GAS CHROMATOGRAPHY STUDIES

Studies by Dr. T. C. Dorris and Dr. S. L. Burks at Oklahoma State University have shown that some organics present in refinery wastewaters are toxic to fish, and some organics are refractory to biological degradation.[2] These organic chemicals persist in lakes and streams for long periods of time. It is also noted that a refractory organic cannot be detected by the TOD test that has been used in the past to evaluate the efficiency of treatment systems. Tests such as TOD, TOC, and COD are much more realistic for the indication of organics in a water sample. Of these tests, TOC is the one that measures only organics.

The laboratory researchers must go further and use sophisticated methods for actually identifying and characterizing the refractory organics so that engineers will know the type of organics that must be removed, thus designing treatment systems to improve the quality of water discharged to the receiving streams.

Carbon treatment is a relatively efficient method for removing organics from refinery wastewater and may be used as a secondary or tertiary treatment system to reduce the BOD of effluent water to a very low level. In studies to learn more about carbon treatment, carbon columns were installed at a petroleum refinery wastewater treatment plant at a point immediately after the API separator and at a point after the final clarifier for the activated sludge treatment unit. The carbon removed from these columns was extracted with several organic solvents to determine which solvents were most efficient and to provide samples of the organics for silica gel, gas chromatographic (GC), infrared, and GC-mass spectrometric analyses.[3]

About 100 ml of an air dried carbon sample were weighed and placed directly into the soxhlet extraction apparatus with a glass wool plug at the bottom to prevent the carbon from getting into the siphon tube. Three hundred ml of solvent were used in the flask. The rate of solvent reflux was adjusted to give four cycles per hour, and the extraction was continued for 22 hours. After 22 hours, the solvent-oil mixture was cooled to room temperature and filtered through a 10 cm depth of anhydrous sodium sulfate crystals contained in a 20 mm by 25 cm glass tube to dry the mixture and remove any carbon particles that might be present. The dried solvent-oil mixture was then distilled through a 20 mm diameter column containing 12 cm of glass beads until the volume remaining in the flask was slightly less than 50 ml. The concentrated solvent-oil mixture was measured into a sample vial, and the volume adjusted to exactly 50 ml with rinsings from the flask.

A gas chromatograph, with a flame detector and an electronic integrator, was used to determine the amount of oil extracted with each solvent. A 1/8-inch by 20-foot stainless steel column, packed with 70/80 mesh Chromosorb G, AW-DMCS, with 5% OV-101 stationary phase, was programmed to hold at room temperature for four minutes with the oven lid open, then the lid was closed and the program proceeded from 35° to 65° C at 8 degrees per minute and from 65° to 350° C at 6 degrees per minute. The temperature was held at 350° C for up to 20 minutes, if it appeared necessary to elute all of the sample. Injector and detector temperatures were about 370° C.

A solution of 3 gm of diesel fuel diluted to 50 ml with solvent was used as a standard since it was available, although an oil with a higher aromatic content would have been more desirable. The total area of the chromatogram of the standard, excluding the solvent peak and correcting for baseline drift near the end of the chromatogram, was compared with the total areas obtained from the 50 ml samples of extract. Data obtained from the carbon extractions and GC analyses are shown in Table 13.

Chloroform, benzene, and methylene chloride showed about the same efficiency for extracting oil from the carbon, while hexane and methanol were less efficient. Figures 10 through 14 show the chromatograms obtained on the extracts from API carbon using the five different solvents. Comparison of the benzene, methylene chloride, and chloroform extracts (Figures 10, 11, and 14) shows that the oils extracted with these solvents were almost identical in composition. However, chloroform showed an advantage in the recovery of one low boiling compound which was an appreciable amount of the sample as indicated from the size of the peak. This peak had a retention time of 11.3 minutes which corresponds to the retention time of benzene. This peak could not be seen when benzene was used as the solvent, and shows at a much lower concentration in the methylene chloride extract.

Chloroform was used as the solvent for extracting a sample of carbon that had been used to treat effluent water from the final clarifier of the activated sludge treatment system. This carbon is referred to as FC carbon, and the resultant chromatogram is shown in Figure 15. The FC carbon contained about 1/3 as much oil as the API carbon. A sample of new carbon also was extracted with chloroform to determine whether the new carbon contained any extractable material. This extract contained no measurable oil, as illustrated by Figure 16. This figure also serves as a good illustration of the purity of the chloroform used as the solvent. Figure 17 is a chromatogram of the standard mixture used to quantitate area data in terms of grams of oil extracted.

The API carbon extract and FC carbon extract were each separated into three fractions by selective elution and desorption from silica gel. The columns were pre-wet with hexane and as the last drop of hexane disappeared into the surface of the gel, the sample-gel mixtures in the 10 ml beakers were emptied into their respective columns. The samples were then fractionated by eluting the saturates with 10 ml of hexane, the aromatics with 10 ml of benzene, and finally desorbing the polar fraction with methanol. Each of the fractions was then reduced in volume to 0.5 ml by evaporating the solvents with a gentle stream of air.

Gas chromatography was used to obtain an estimate of the amount of saturates, aromatics, and polar material in each of the samples. The oil extracted from the FC carbon contained such small amounts of saturates and aromatics that it was necessary to increase the sensitivity of the GC by a factor of 10 to obtain measurable areas. These areas were then divided by 10 to get back to the same basis as the area measurements on the polar fraction. The results are tabulated in Table 14.

These data indicate that the activated sludge treatment system has reduced the saturates and aromatics to very low levels in the final clarifier effluent but has been relatively ineffective in removing some of the polar type organic compounds.

Figures 18, 20, and 22 are chromatograms of the saturate, aromatic, and polar fractions obtained by the silica gel separation of the oil from API carbon. Figures 19, 21, and 23 are chromatograms of the saturate, aromatic, and polar fractions obtained by the silica gel separation of the oil from FC carbon.

There was insufficient time for complete GC-MS identifications, but Table 15 lists some of the compounds and types that have been found to date in the saturate, aromatic, and polar fractions. The organic structures shown in the table are those normally found in petroleum and petroleum products, but it is noted that three sulfur compounds were found in the aromatic fraction of the FC carbon extract. It may be that these compounds are not biologically degraded as much as the aromatics and are a more significant part of the aromatic fraction after biological treatment.

The polar fractions could not be analyzed by GC-MS because of the inability of the gas chromatograph to separate the complex mixture. The complexity of the mixture is illustrated in Figures 22 and 23 by the lack of baseline separation. Differences in the two chromatograms indicate that some of the components have been degraded in the activated sludge treatment system. It is probable that the reduction in phenolic compounds, that is known to occur, would account for some of the differences noted in the chromatograms.

Infrared scans on the polar fractions were almost identical. Functional groups noted were OH and C=O, and CH_2 and CH_3 adsorption bands indicate aliphatic type structures. Further work must be done on the polar fractions to identify a number of the individual compounds in the mixture so that an assessment of their toxicity can be made and treatment methods developed to remove these compounds.

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BIOGRAPHIES

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DISCUSSION

Bill McCarthy: When you used solvent extraction for recovering your adsorbent components, could you give us an idea of what efficiency or recovery you got?

Leon H. Myers: No I can't, because we did not attempt a mass balance; however, the quantitative value of three solvents produced similar results. The quantity recovered agrees with the projected isotherm loading.

Bill McCarthy: Do you think solvent regeneration might be a viable process?

Leon H. Myers: Yes, I do believe it is both feasible and viable, and this is determinant on the mixtures of hydrocarbons to be removed. In some cases, particularly with light hydrocarbons, steam regeneration might be the most viable regeneration process. Neither of these alternate regeneration modes have been thoroughly proven.

Table 1. CONTROLLED CONDITIONS FOR ISOTHERM STUDY

1. 325 mesh (pulverized)
2. 200 ml sample
3. 1 hour contact
4. 0.05, 0.20, 0.50, 1.0 gm carbon
5. 100 rpm agitation
6. 23° C temperature
7. 75 mg/l TOC
8. pH 7.4

Table 2. ADSORPTION DATA FOR ELEVEN ACTIVATED CARBONS

Carbon Sample	mg/l TOC Adsorbed on 1 gm Carbon	
	Pulverized	Granular
1	50	38
2	60	37
3	56	37
4	57	48
5	56	29
6	52	31
7	47	41
8	51	47
9	49	38
10	35	13
11	46	34

Table 3. CONTACT TIME ADSORPTION

	Time in Minutes			
Gm Carbon (Blank)	20 (206 mg/l)*	40 (260 mg/l)*	60 (260 mg/l)*	180 (260 mg/l)*
0.1	124	96	82	101
0.5	63	45	51	73
1.0	57	47	106	45
2.0	55	52	77	34
5.0	56	54	50	24

* Results are expressed as mg/l filtrable total organic carbon.

Table 4. ANTHRAFILT FILTRATION ORGANIC CARBON REMOVAL

	TOC	Turbidity
Charge	255 mg/l	11.0
After 5 minutes (0.3 gal.)	220 mg/l	
After 1 hour (3.2 gal.)	210 mg/l	
After 2.5 hours (7.9 gal.)	206 mg/l	2.75

Table 5. MINI-COLUMN TOC RESULTS

Date	Final Clarifier Effluent*	Anthrafilt Effluent*	Columns					
			A-1*	B-1*	A-2*	B-2*	A-3*	B-3*
3/17	35	31	13	9	9	10	7	12
3/18	33	34	11	11	10	12	10	18
3/19	48	40	13	16	14	14	8	12
3/20	37	48	17	23	22	16	11	22
3/21	35	38	18	19	17	25	16	32

* All concentrations are mg/l TOC.

Table 6. COMPARISON OF MINI-COLUMN TOC REMOVAL EFFICIENCY

Date	Percentage Removals					
	A-1	B-1	A-2	B-2	A-3	B-3
3/17	58	71	71	68	77	62
3/18	68	68	71	65	71	47
3/19	68	60	65	65	80	70
3/20	65	52	54	67	77	54
3/21	53	50	55	34	58	16
Average	62	60	63	60	73	50

Table 7. TOC RESULTS OF MINI-COLUMN UPFLOW MODE

Date	Final Clarifier Effluent*	Anthrafilt Effluent*	Columns 1*	2*	3*	4*	5*
3/24	50	38	19	12	11	13	13
3/25	35	33	17	13	10	10	9
3/26	41	33	20	24	18	13	12
3/27	38	35	17	19	17	13	10

* All concentrations are mg/l TOC.

Table 8. PERCENTAGE REMOVAL OF TOC FOR UPFLOW MODE

Date	Columns 1	2	3	4	5
3/24	50	68	71	66	66
3/25	48	61	70	70	73
3/26	39	27	45	61	64
3/27	51	46	51	62	71
Average	47	51	59	65	69

Table 9. REFINERY PROCESS DATA

Capacity	30,000 BPSD
API Class	B
Wastewater Volume	18 gal. per minute
Refinery Processes:	1. Crude Distillation 2. Crude Desalting 3. Vacuum Crude Distillation 4. Fluid Cat Cracking 5. HF Alkylation 6. Hydro Cracking 7. Catalytic Reforming 8. Asphalt Production

Table 10. REFINERY WASTEWATER TREATMENT RESULTS

Parameter	Median Values			
	API Separator (mg/l)	Bio-Treated (mg/l)	Carbon-Treated (mg/l)	Bio-Carbon Treated (mg/l)
BOD_5	97	7	48	3
COD	234	98	103	26
TOC	56	30	14	7
Oil and Grease	29	10	10	7
Phenols	3.4	0.01	0.004	0.001
Chromium	2.2	0.9	0.2	0.2
Copper	0.5	0.1	0.03	0.05
Iron	2.2	3.0	0.3	0.9
Lead	0.2	0.2	0.2	0.2
Zinc	0.7	0.4	0.08	0.15
Sulfide	33	0.2	39	0.2
Ammonia	28	27	28	27
Cyanides	0.25	0.2	0.2	0.2
Turbidity*	26	17	11	5
Color**	30	15	15	1

* Turbidity given in Jackson Turbidity Units.

** Color given in color units.

Table 11. CARBON ADSORPTION CAPACITY

	Capacity Lbs TOC Adsorbed Per Lbs Carbon
Isotherm Study	0.12
API Separator Effluent Carbon Column	0.31

Table 12. CARBON REGENERATION ACTIVITY ANALYSIS

	Iodine No.	Molasses No.
Virgin Carbon	1010	216
API Separator Carbon	906	405
Final Clarifier Carbon	991	304

Table 13. SOLVENT EXTRACTION EFFICIENCY DATA

Carbon Identification	Solvent	Grams Carbon	Grams Oil Extracted	Gram Oil/ Gram Carbon
API	Chloroform	49.3008	5.04	0.102
API	Benzene	50.6917	5.01	0.099
API	Methylene Chloride	54.5660	5.44	0.100
API	Methanol	56.3179	3.71	0.066
API	Hexane	55.3762	4.03	0.073
FC	Chloroform	56.6447	1.95	0.034
NEW	Chloroform	44.6169	0.00	0.000

Table 14. COMPOSITION BY TYPES OF ORGANICS

Organic Type	Oil from API Carbon	Oil from FC Carbon
Saturates	11.1%	0.2%
Aromatics	24.7	1.3
Polar Material	64.2	98.5
	100.0	100.0

Table 15. COMPOUND TYPES INDICATED BY GC-MS

	API Carbon Extract	FC Carbon Extract
Saturate Fraction	C_8H_{16}	
	C_9H_{16}	
	C_9H_{18}	
	$C_{10}H_{20}$	
	$C_{12}H_{24}$	
	C_8 through C_{29} n-paraffins	
Aromatic Fraction	Ethylbenzene	Ethylbenzene
	Xylenes	Xylenes
	C_9 Benzenes	C_9 Benzenes
	C_{10} Benzenes	C_{10} Benzenes
	Naphthalene	C_7H_8S
	C_{11} Benzenes	$C_7H_{10}S$
	C_{11} Naphthalene	C_9H_8S
	C_{12} Naphthalene	
	C_{13} Naphthalene	
Polar	Phenol	
	Hydroxytoluene	

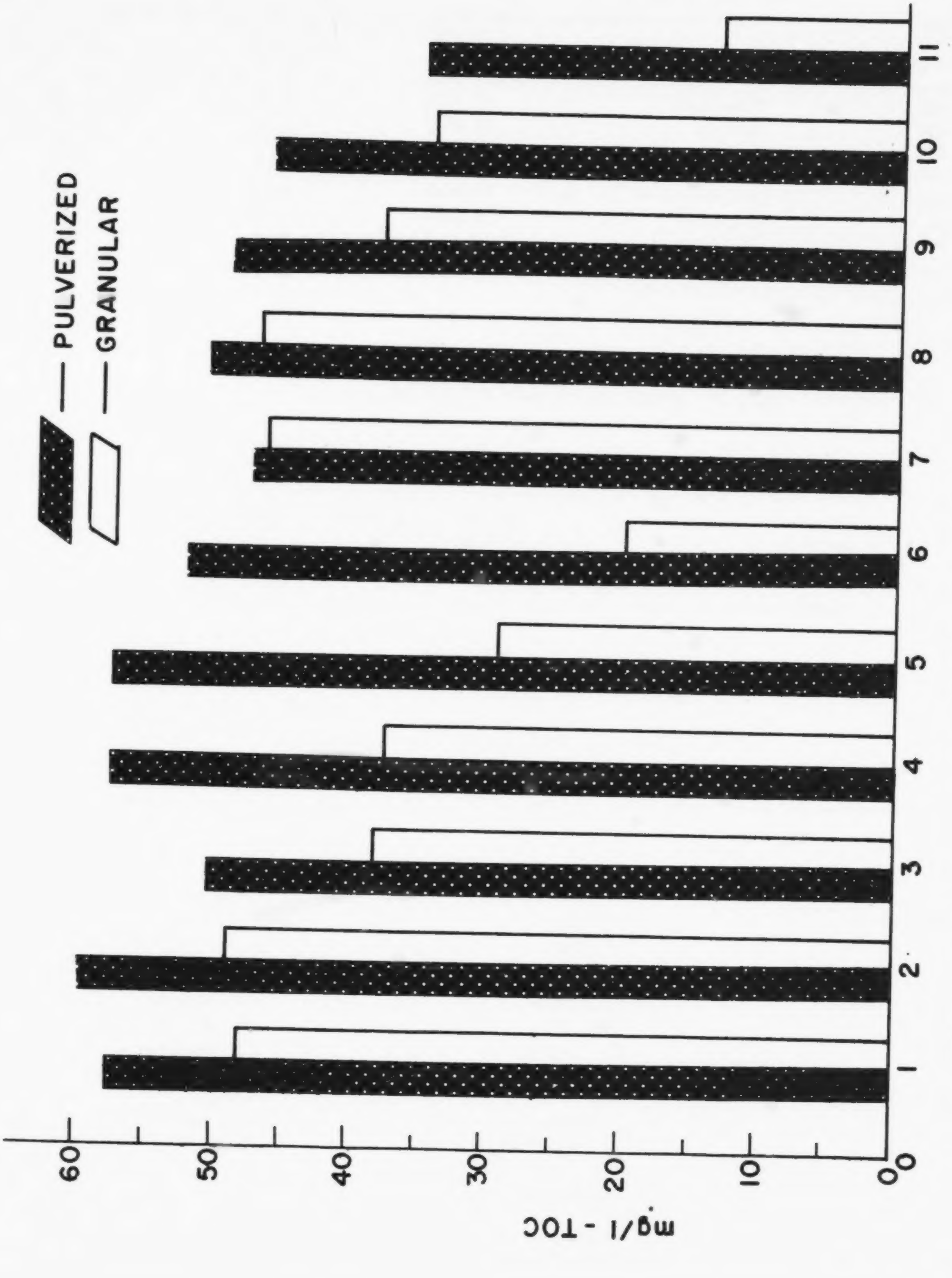

PULVERIZED
GRANULAR
mg/l - TOC
0
10
20
30
40
50
60
0
1
2
3
4
5
6
7
8
9
10
11
CARBON SOURCES

FIGURE - I

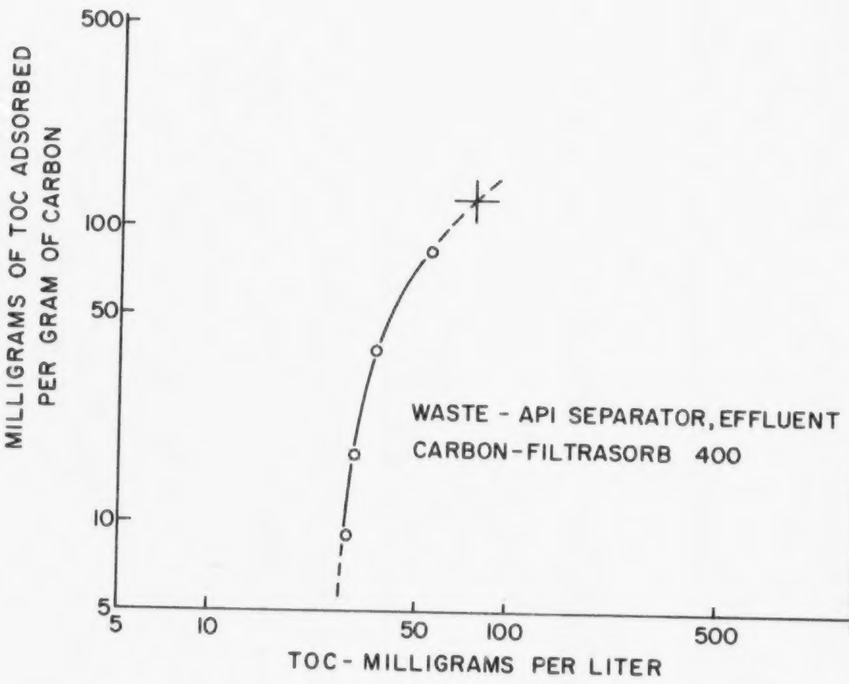


FIGURE 2 - ADSORPTION ISOTHERM

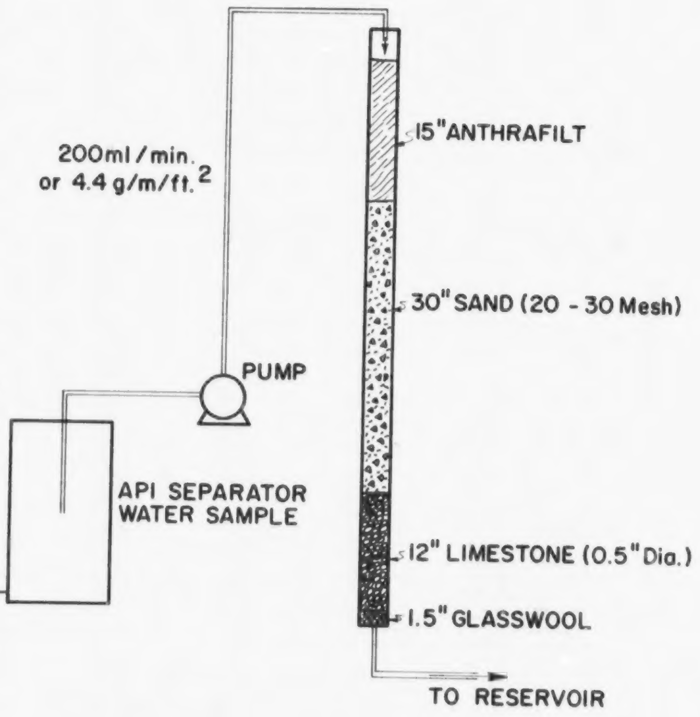

200ml / min.
or 4.4 g/m/ft.^{2}
PUMP
API SEPARATOR
WATER SAMPLE
15" ANTHRAFILT
30" SAND (20 - 30 Mesh)
12" LIMESTONE (0.5" Dia.)
1.5" GLASSWOOL
TO RESERVOIR

FIG. 3- MULTI - MEDIA FILTER

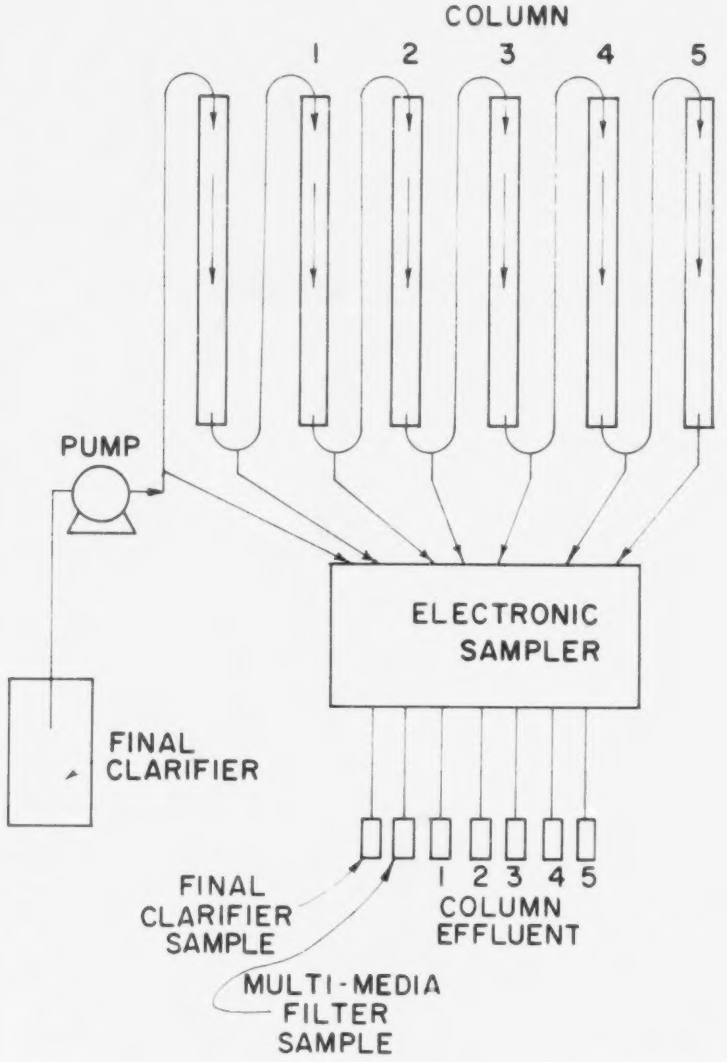

COLUMN
1
2
3
4
5
PUMP
ELECTRONIC SAMPLER
FINAL CLARIFIER
1 2 3 4 5
COLUMN EFFLUENT
FINAL CLARIFIER SAMPLE
MULTI-MEDIA FILTER SAMPLE

FIG. 4 - MINI COLUMN SYSTEM

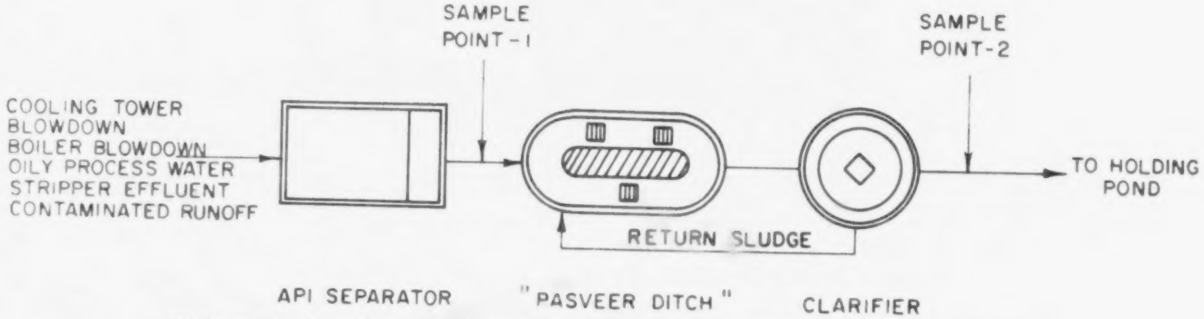

SAMPLE POINT-1
SAMPLE POINT-2
COOLING TOWER BLOWDOWN
BOILER BLOWDOWN
OILY PROCESS WATER
STRIPPER EFFLUENT
CONTAMINATED RUNOFF
TO HOLDING POND
RETURN SLUDGE
API SEPARATOR
"PASVEER DITCH"
CLARIFIER

FIGURE 5 - REFINERY WASTE WATER TREATMENT SYSTEM

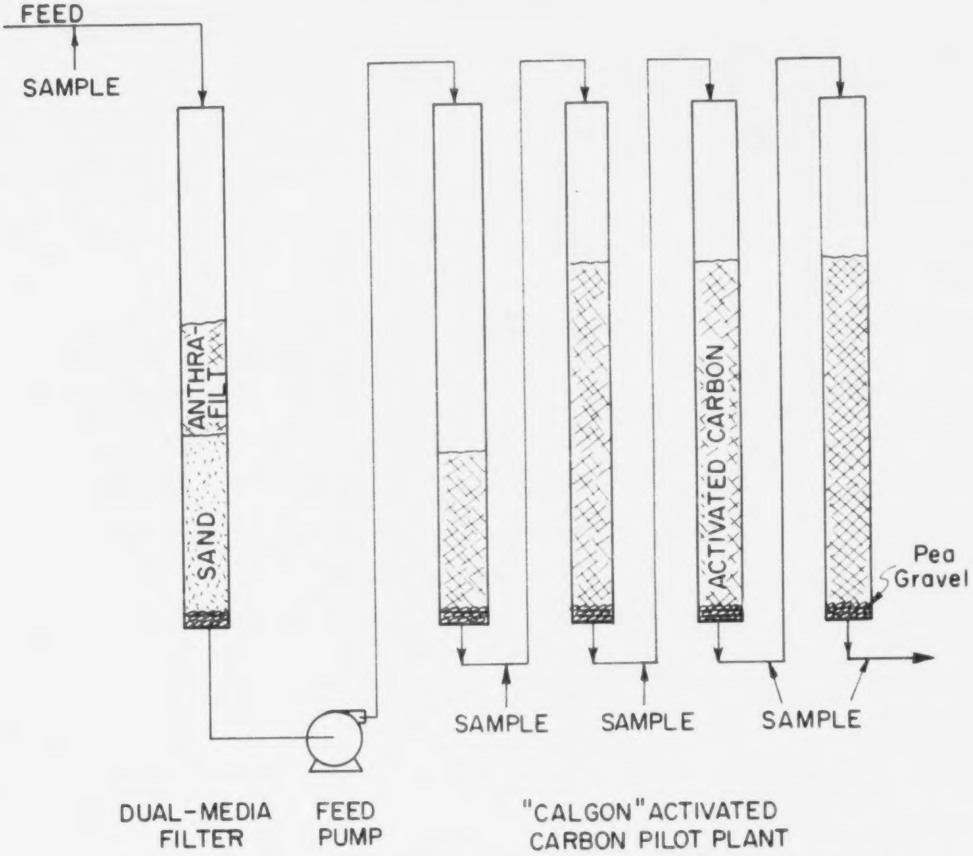

FEED
SAMPLE
ANTHRA-FILT
SAND
ACTIVATED CARBON
Pea Gravel
SAMPLE
SAMPLE
SAMPLE
SAMPLE
DUAL-MEDIA FILTER
FEED PUMP
"CALGON" ACTIVATED CARBON PILOT PLANT

FIGURE 6 - ACTIVATED CARBON PILOT PLANT FLOW DIAGRAM

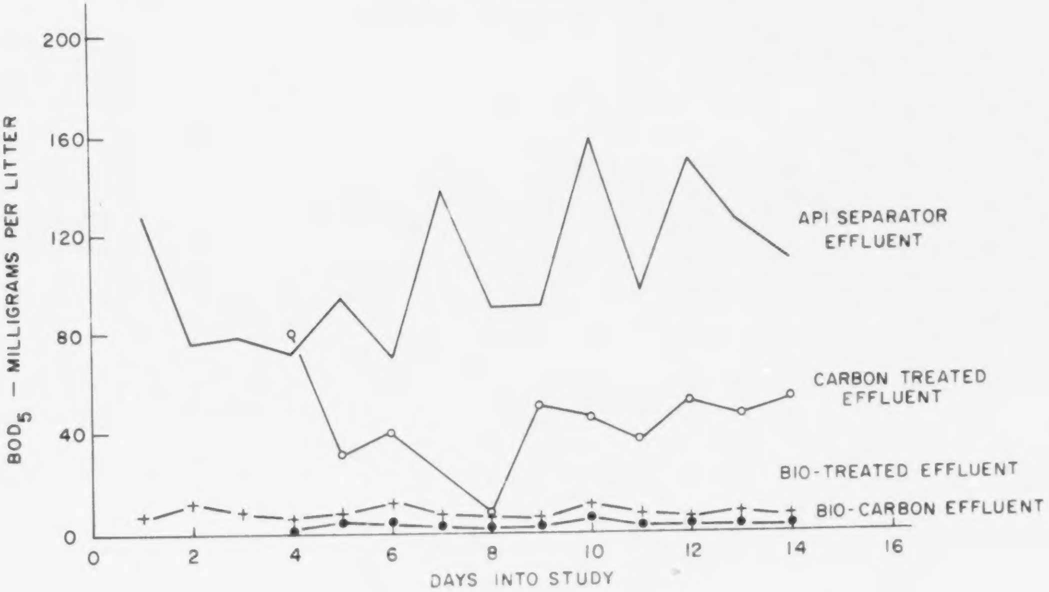


FIGURE 7 - TREATMENT RESULTS, BOD

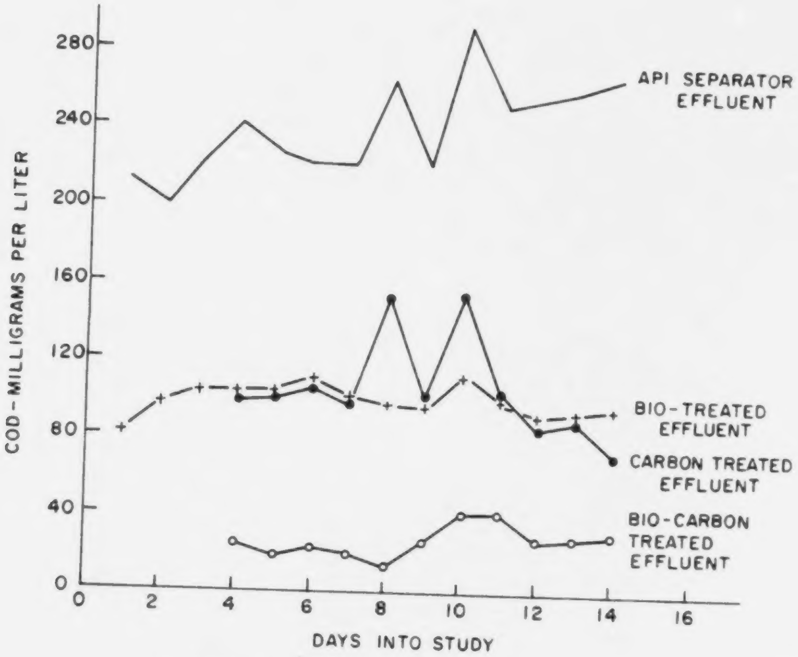


FIGURE 8 - TREATMENT RESULTS, COD

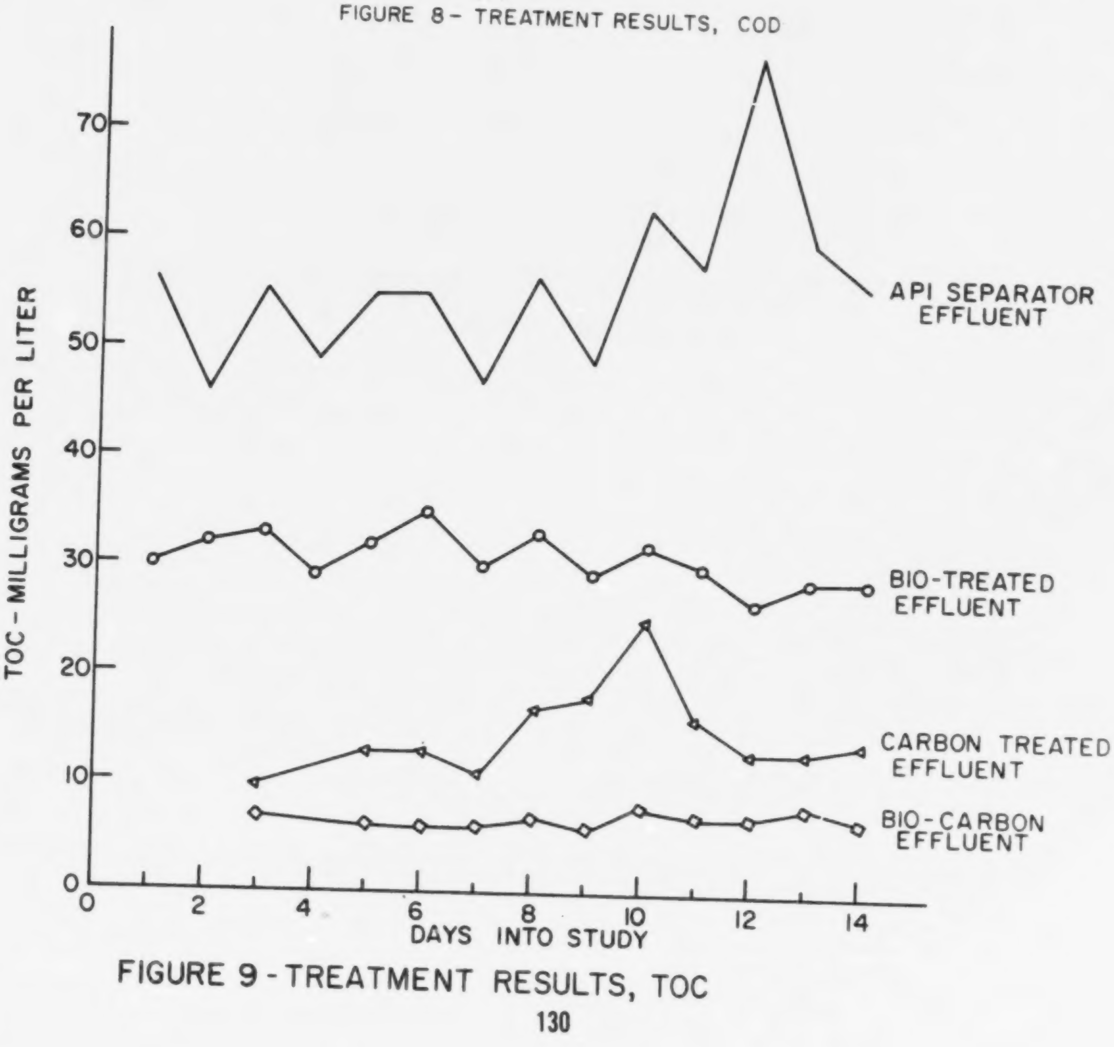


FIGURE 9 - TREATMENT RESULTS, TOC

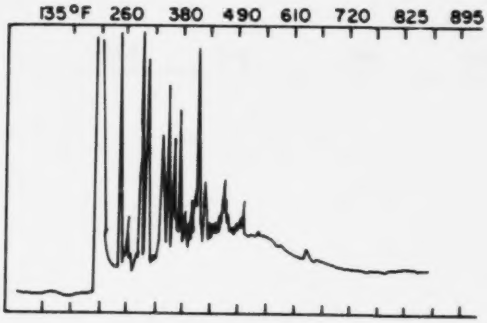


FIGURE 10 – BENZENE EXTRACT OF API CARBON

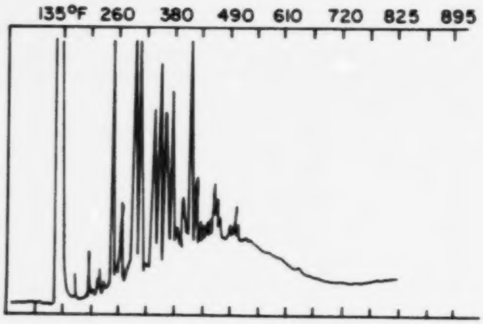


FIGURE 11 – METHYLENE CHLORIDE EXTRACT OF API CARBON

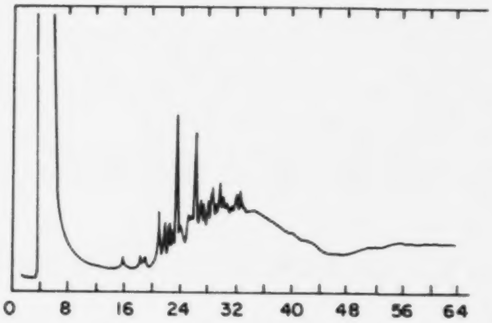


FIGURE 12 – METHANOL EXTRACT OF API CARBON

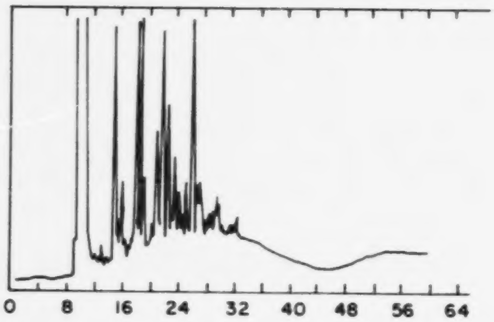


FIGURE 13 – HEXANE EXTRACT OF API CARBON

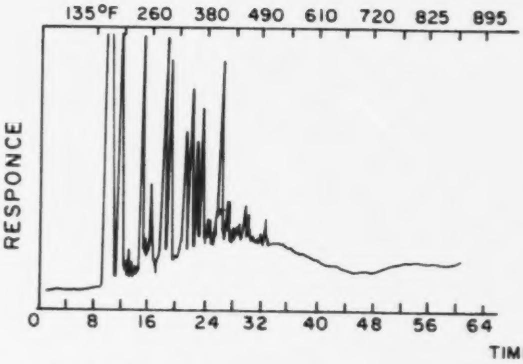


FIGURE 14 – CHLOROFORM EXTRACT OF API CARBON

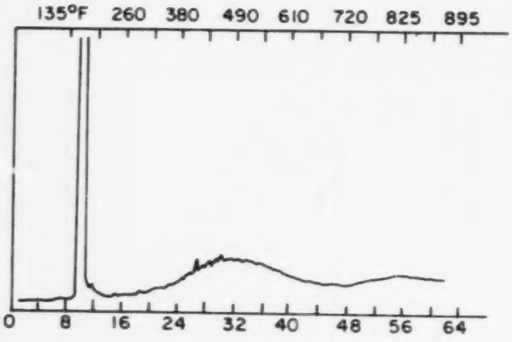


FIGURE 15 – CHLOROFORM EXTRACT OF FC CARBON

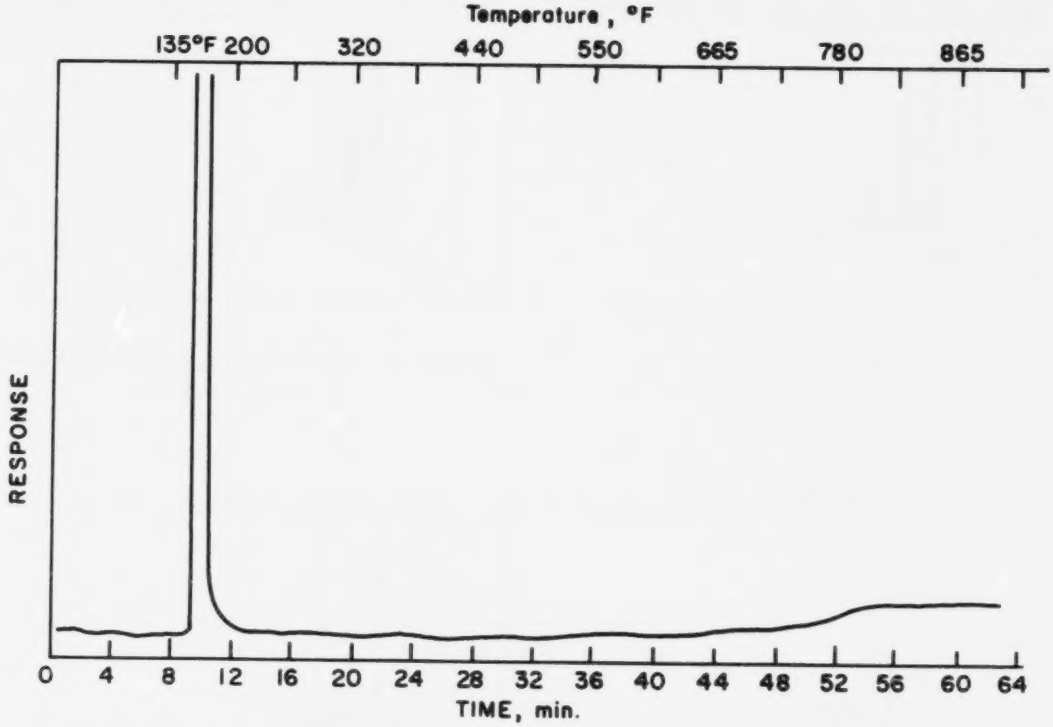


FIGURE 16 - CHLOROFORM EXTRACT OF NEW ACTIVATED CARBON

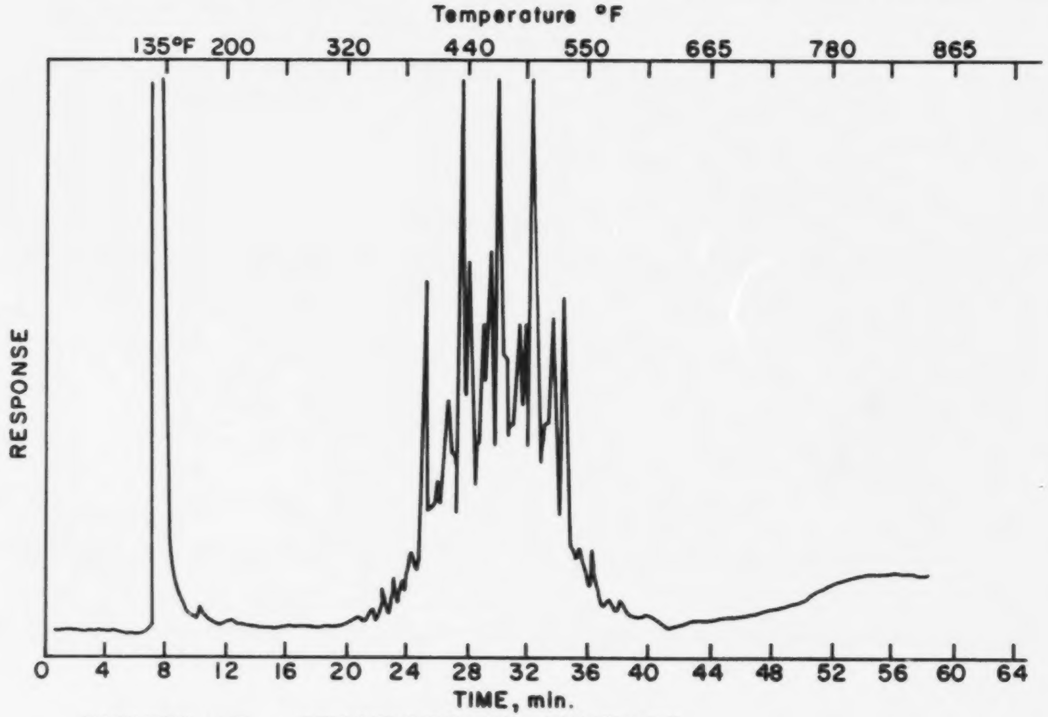


FIGURE 17 - STANDARD OIL MIXTURE

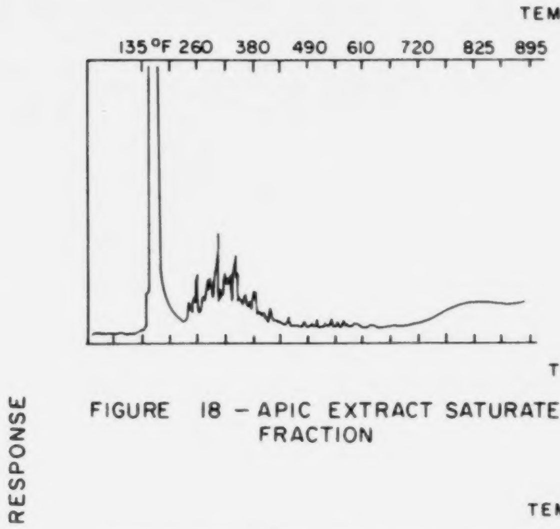


FIGURE 18 – APIC EXTRACT SATURATE FRACTION

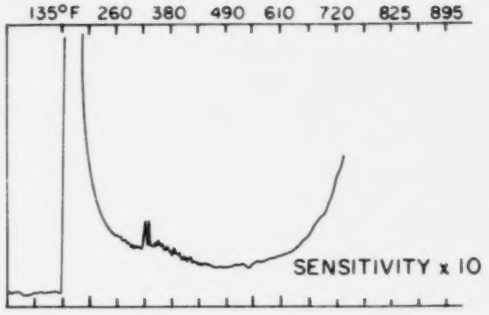


FIGURE 19 – FCC EXTRACT SATURATE FRACTION

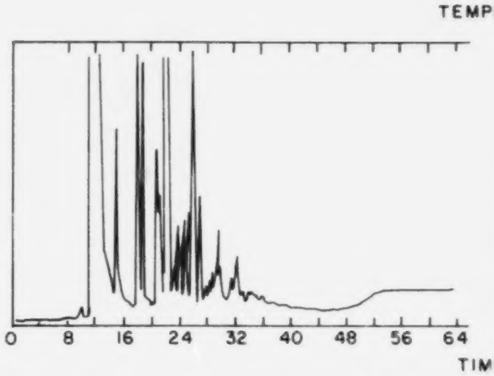


FIGURE 20 – APIC EXTRACT AROMATIC FRACTION

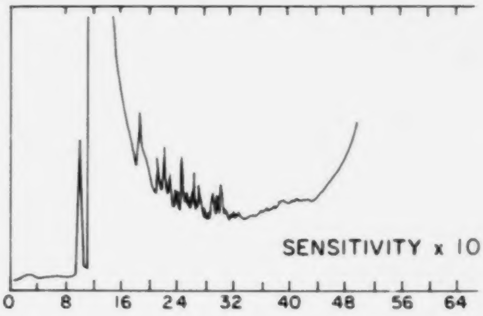
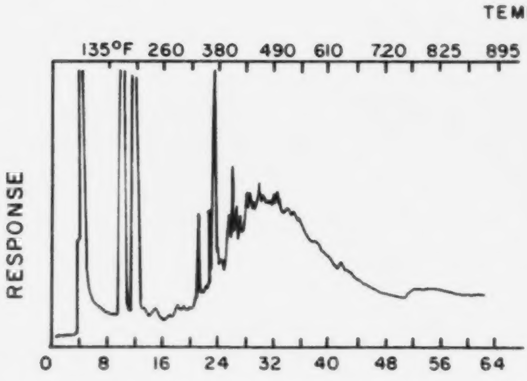


FIGURE 21 – FCC EXTRACT AROMATIC FRACTION



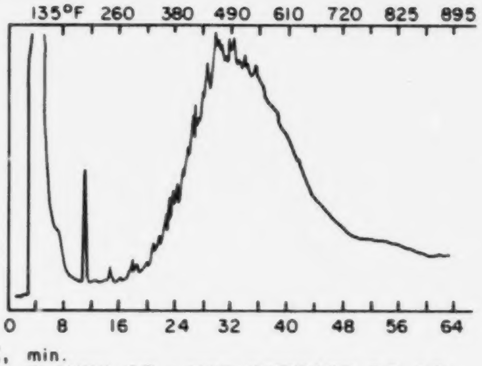


FIGURE 22 – APIC EXTRACT POLAR FRACTION

FIGURE 23 – FCC EXTRACT POLAR FRACTION

SECTION 4

Powdered Activated Carbon Pilot-Scale Studies

"COMBINED POWDERED ACTIVATED CARBON - BIOLOGICAL TREATMENT: THEORY AND RESULTS"

Francis L. Robertaccio, Senior Engineer
E.I. duPont de Nemours & Co., Inc.
Wilmington, Delaware

The purposes of this paper are: to acquaint you with an overview of some of the theoretical aspects of the combined powdered activated carbon-biological treatment process, and to present recent start-up experiences and results from the 1.5×10^5 M^3/day installation based on the process at the Du Pont Chambers Works Plant in Deepwater, New Jersey.

Pact is Du Pont's name for a patented process for purification of sewage and/or industrial wastewater which comprises subjecting the wastewater to an aerobic biological treatment process in the presence of powdered activated carbon (1) (Figure 1). The aerobic biological treatment vessel (s) can have many geometric configurations. Single or multiple reactors can be used. The reactors can be plug flow, completely mixed, or somewhere in between. Powdered activated carbon addition is compatible with activated sludge, contact stabilization, or aerated lagoon systems; that is, any process in which the carbon can be suspended. The rate of powdered activated carbon addition for a given wastewater is a function of the effluent quality desired. When the rate of addition is expressed in terms of weight of carbon added per unit volume of incoming wastewater, the rate becomes a function of the type of carbon used.

In addition, certain internal process controls such as the solids retention time, or sludge age, can be changed to influence the rate of application of a given type of carbon to produce a desired result. (2) Some of these relationships are illustrated in Figure 2. Here sludge age and carbon dose are shown as variables affecting effluent quality as measured by the total organic carbon (TOC) test. All data points represent treatment conditions by which the effluent BOD of the industrial wastewater tested was reduced to negligible concentration. The effluent TOC is shown to be reduced by an independent increase in either the sludge age or the carbon dose. Note that the improvement in effluent quality, by increasing sludge age, is less apparent when carbon is absent. We have long postulated this phenomena results because the adsorbed microorganisms have the sludge age rather than the relatively shorter hydraulic detention time to biodegrade adsorbed and difficult-to-degrade molecules. It is important to recognize the economic advantage associated with the ability to biodegrade these materials in the biological reactor as an inherent advantage of the process.

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The alternative for this type of effluent quality improvement is a more expensive add-on granular carbon adsorption step.

Table 1 illustrates the effectiveness of using carbon as an adsorbent in a biological reactor.(3) The table shows the dissolved organic carbon (DOC) removal from a PACT unit and comparable data from a biological unit. Also shown is the combined removal obtained from a separate adsorption of the biological unit effluent using the same type and quantity of carbon used in the PACT unit. The same carbon combined with bacteria in the PACT unit removed more DOC and exceeded the quantity expected from separate isotherm determinations.

Of course, as more molecules are biodegraded, adsorption sites are filled with molecules that are more biorefractory and a more rigorous form of regeneration is needed if the spent carbon is to be reused. Alternatively, more active carbons (i. e., higher surface area) can be used in throw away doses. Economic considerations grouped as various capital and operating expenses dictate the choice. To some extent the economics are strongly influenced by the carbon usage rate, however, site specific factors such as the local costs of alternative sludge disposal methods must be considered. At the PACT treatment facility for Chambers Works we will thermally regenerate carbon from PACT sludge but wet oxidation can also be used.

The heart of the PACT system is a matrix of microorganisms and powdered activated carbon. Figure 3 shows the matrix.(2) The photo on the left is powdered activated carbon in the water; the photo on the right the PACT matrix. The PACT matrix has some interesting properties.

First, the carbon acts as a weighting agent. Sludge settling rates are vastly improved as illustrated in the series of pictures in Figure 4. Activated sludge and PACT mixed liquor were taken from treatability units operating on the same wastewater at the same sludge age. The series of photographs are taken at different elapsed settling times shown on the timer in the background. Note that the PACT sludge settles better and has a clearer supernatant. The PACT sludge also compacts very well. The PACT sludge had a mixed liquor suspended solids concentration of 7700 mg/l (about 65% carbon) and a sludge volume index of 20 cc/g. The activated sludge had a mixed liquor concentration of 2400 mg/l and a sludge volume index of 46. We feel that the improved sludge settling, achieved by simple carbon addition can result in the processing of more wastewater through existing hydraulically overloaded treatment plants. This is often a viable alternative to rather expensive capital equipment expansion programs to accomplish similar results. Of course, carbon addition will improve effluent quality at the same time. A new treatment plant can incorporate this advantage in its design by substantially reducing the size of secondary clarification. Another illustration of the improved settling of PACT sludge is shown in Figure 5. Here the initial settling velocity of activated sludge is compared at various concentrations to a family of PACT sludge curves at two carbon levels and two temperatures. The numbers on the PACT labeled curves are the application rates for carbon in mg/l.

While on the topic of sludge handling, it should be mentioned that PACT sludge dewaters much more readily than conventional activated sludge. The manifestation of this property is reduced size of sludge dewatering equipment. The need to dewater more sludge as a result of the presence of carbon is offset by reduced cycle times. Figure 6 compares the specific resistance of activated sludge to two PACT sludges at different carbon feed doses.(3)

A second property of the PACT sludge matrix is that it contains an effective adsorbent. We have already explored one aspect of the role of the adsorbent - removal of biorefractory organic compounds - in the discussion of carbon dose and its relationship to sludge age. In that discussion the effluent total organic carbon content was a gross measure of biorefractory material. More specific measures of biorefractory materials which might require control in specific instances include materials contributing to final effluent color, oil and grease, surfactants, chlorinated hydrocarbons, phenols and toxicity to fish or other trophic level measures of toxicity in receiving waters. No matter how you care to measure, or are told to measure these biorefractory materials,it is apparent PACT can control these substances to levels beyond the capability of conventional biological systems. In complex waste situations control of these substances at the PACT treatment plant is often a more viable alternative than biological systems followed by granular activated carbon columns or source treatment.

Sometimes biorefractory materials are as much, or more of a problem within a biological system as they are in its final effluent. Examples include materials toxic or inhibitory to biological reactor microorganisms, materials that are periodically present in high concentrations (shock loads), or materials that cause severe foam, odor, or bulking sludge. Unlike post-biological separate granular activated carbon treatment, the presence of carbon in the aerator often controls these in-process problems as well as those normally associated with the biologically treated effluent. Over the years, we have had a difficult time sustaining bench scale biological treatability units on Chambers Works wastewaters due to the periodic presence of toxic or inhibitory materials.(4) However, PACT treatability units operated in parallel did not experience similar upsets. As a result of this property of the PACT process the full scale PACT facility at Chambers Works has no upstream equalization. We have even spiked Chambers Works wastewater with various toxic substances including pentachlorophenol (190 l/min. pilot plant test) and found the PACT system can sustain efficient operation when the conventional biological system completely fails. Ferguson, et al , reported similar findings in shock loading tests involving trichlorophenol.(5)

There are two intertwining reasons to consider any waste treatment process: technical merits and economics. We have touched upon the technical merits of the PACT process and summarized them in Table II. In most instances any one of the technical merits may be sufficient reason to consider PACT. In most instances a number of technical merits must be simultaneously applied to the consideration of the process at a specific site. The resulting matrix of reasons results in a difficult appraisal of the full value of the use of the PACT process versus alternative processes. Some of the economic considerations are shown in Table III. At Du Pont we are convinced PACT is a versatile, economic and technically viable process. We have about 100 man years experience in PACT process research and development. At the Chambers Works facility which will be described next, we feel PACT represents a \$7 million capital savings and a \$5 million/year operating cost savings (1972 dollars) over the next best alternative which was granular carbon treatment followed by activated sludge.(6)

The full scale PACT facility at Chambers Works has been in a start-up phase since mid-November 1976, and it proceeded smoothly through the coldest winter in decades. The liquid train is on line and the solids handling train is expected to be fully operational fairly soon. During March 1977 a half full flowrate test, and during early May a full flowrate test were conducted. This portion of this paper will highlight the start-up operation and describe results of the tests.

Figure 7 shows the major components of the PACT portion of the Chambers Works treatment plant. Construction of the PACT facility started in February 1974 and was completed in December 1976 at an estimated capital cost of \$22.5MM. Primary effluent is split equally to each of three 15MM liter aeration tanks as is the recycled PACT sludge. Five 1,000 hp blowers supply air to static mixers in the aerators. Effluent from the aerators is conveyed to the clarifier flowsplitter and then to two secondary clarifiers. Treated effluent (overflow) is discharged to a basin and then to the Delaware River. Secondary clarifier underflow is returned to the aeration tanks via two 2 meter screw pumps. This part of the system constitutes the "liquid train" and includes feed and unloading facilities for carbon, phosphoric acid and polymer.

Waste sludge can be removed from either the mixed liquor or recycle lines and is pumped to a sludge thickener where it is settled to 7 ± 2 weight percent solids. The thickener underflow serves as a feed stream for the filter press which is designed to produce a 35 weight percent dry solids PACT cake. The cake is mechanically conveyed to a five hearth furnace where it is dryed, the biomass incinerated, adsorbed organics pyrolyzed and the powdered carbon in the sludge regenerated for reuse. The furnace off-gases pass through two scrubbers and an afterburner before being discharged to atmosphere. The dry, regenerated carbon recovered off the bottom hearth is slurried, acid washed, and returned to the carbon feed tanks for recycle to the process. No waste sludge is produced. This part of the system is called the "solid train".

The liquid train startup became evident in November 1976 when 2.7×10^5 kg of powdered carbon and 2.0×10^5 kg of bacterial solids were added to one aerator. Water temperature at the time was 11-15°C. During January a second aerator and clarifier were brought on line. During February the carbon regeneration startup began and during March the sludge press was brought on line. The more important operating problems encountered and solved during startup have been presented in a recent paper by Flynn.(7) The problems were of the type found with the startup of a conventional activated sludge process, that is, they were not at all related to the uniqueness of the PACT process. These problems went through the classic problem solving stages - initial definition, questioning of assumptions, hypothesis forming, reobservation of the problem in some cases, implementation of a solution and feedback on the success of the solution.

In March a half-full flowrate test was conducted. Table IV compares operating conditions, feed and effluent quality for the full scale PACT facility and various bench scale controls. The effluent color and dissolved organic carbon (DOC) are important control parameters. During this test, flowsheet dosages of virgin carbon (regenerated carbon not available at this date) reduced effluent DOC to 20 ppm (43 ppm goal) for the last seven days of the test and an average of 36 ppm for the entire test. Effluent color was 310 (540 goal) despite the feed color being 42% over design. The full scale, half-flow test results compare favorably with the PACT bench scale control. This table also presents insight into the improvement in effluent quality offered by PACT. Note the marked decrease in effluent DOC and color in the PACT full scale or bench scale units versus the biological bench scale unit.

In early May a full flowrate test was conducted. Table V presents operating conditions, feed and effluent quality for the test. The effluent color and dissolved organic carbon again met goals despite the feed color being 108% over design. Once again this test was conducted using virgin carbon.

In summary, this paper has presented an overview of some of the theoretical aspects of the combined powdered activated carbon-biological treatment process (PACT) and updated recent startup experiences from the 1.5 x 10^5 M^3/day installation based on this process at the Du Pont Chambers Works. This process is a versatile, viable wastewater treatment technology; we expect its use to become an accepted solution to a variety of existing and future wastewater treatment problems.

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2. Flynn, B. P., F. L. Robertaccio and L. T. Barry, "Truth or Consequences: Biological Fouling and Other Considerations in the Powdered Carbon - Activated Sludge System". Presented at the 31st Annual Purdue Industrial Waste Conference, West Lafayette, Indiana, May 5, 1976
3. Heath, H. W., "Combined Activated Carbon-Biological ("PACT") Treatment of 40 MGD Industrial Waste" presented to Symposium on Industrial Waste Pollution Control at ACS National Meeting, New Orleans, LA., March 24, 1977
4. Robertaccio, F. L., D. G. Hutton, G. Grulich and H. L. Glotzer, "Treatment of Organic Chemical Wastewater with the Du Pont PACT Process". Presented at A. I. Ch. E. National Meeting, Dallas, Texas, February 1972
5. Ferguson, J. F., G. F. P. Keoy, M. S. Merrill and A. H. Benedict "Powdered Activated Carbon - Biological Treatment: Low Detention Time Process" presented at the 31st Annual Purdue Industrial Waste Conference, West Lafayette, Indiana, May 4, 1976
6. Flynn, B. P. and L. T. Barry "Finding a Home for the Carbon: Aerator (Powdered) or Column (Granular)". Presented at the 31st Annual Purdue Industrial Waste Conference, West Lafayette, Indiana, May 1976
7. Flynn, B. P. "Operating Problem Solving During a Secondary-Tertiary Treatment Plant Start-Up". Presented at 11th Mid-Atlantic Regional ACS Meeting, University of Delaware, Newark, Delaware, April 22, 1977

DISCUSSION

Ed Sebesta, Brown & Root: What is the design hydraulic loading for secondary clarifiers at the Chambers Works wastewater treatment facility?

Robertaccio and B. P. Flynn, Du Pont: The solid flux rate is designed at 250 lbs. per day per square foot which is kind of high. At that solid flux rate, you should be able to get an underflow concentration of 3-1/2 weight percent. In full scale testing we have been able to generate 7-1/2 weight percent solids which means we could operate without a waste sludge thickener and could feed our filter press directly from our return sludge line. The hydraulic overflow rate is in excess of about 1000 gallons/day/ft.^{2}. We have two secondary clarifiers but could send full flow through one secondary clarifier.

Leonard W. Crame, Texaco: What does the Du Pont PACT process patent mean to the refining industry in terms of using this process?

Robertaccio: Du Pont will license any user of the process. The royalty rate will be reasonable in order to encourage use of the process.

J. E. Rucker, API: Please comment on economics and feasibility of regeneration of powdered carbon from PACT sludge.

Robertaccio: Economics first. We think that powdered carbon can be regenerated for an operating cost of about 5¢ a pound. Capital costs would depend on the size of the facility and the method used to annualize capital costs. At Chambers Works capital costs would add another 5¢ a pound. Now feasibility. We put as much effort into the regeneration part of the Chambers Works facility as we did to the PACT process. The regeneration system is being brought on line. We have had some mechanical problems but we don't expect to have any more trouble solving these as we had solving other problems. Of course, a number of thermal and wet oxidation regeneration equipment manufacturers will tell you they think regeneration of powdered activated carbon from PACT sludge is no problem.

Dave Skamenca, Envirotech: Did you pilot test mixing the powdered activated carbon - biomass mixture with static mixers?

Robertaccio: Yes.

BIOGRAPHY Francis L. Robertaccio

Fran is a senior engineer for the DuPont Company in Wilmington, Delaware. He has 12 years experience in various industrial pollution control positions. He holds a B.S. and M.S. in Chemical Engineering from Clarkson College and a Ph.D. in Environmental Engineering from the University of Delaware. He has authored a dozen papers on industrial pollution control, holds several U.S. and foreign patents and is a member of AIChE and WPCF.

TABLE I - SYNERGISTIC EFFECT ON DOC REMOVAL WITH "PACT"

TRIAL	FEED TO UNITS	BIO UNIT EFFLUENT	BIO UNIT EFFLUENT + BATCH CARBON ADSORPTION(1)	"PACT"(2) EFFLUENT
	DOC, mg/l			
1	183	80	59	44
2	178	70	42	18
3	167	79	55	25

(1) Take 500 cc filtered Bio Unit effluent, add 150 ppm virgin carbon, stir 3 hours at room temperature, filter, and analyze filtrate for DOC

(2) "PACT" unit operating at 20°C with 8.0 day sludge age and 160 ppm carbon addition

TABLE II - REASONS TO CONSIDER PACT

I Existing Biological Treatment Plants

- A. Need to improve effluent quality
    - treatment plant hydraulically overloaded
    - biological treatment unstable
    - odor, foam
    - new, more restrictive effluent limits
    - biological treatment inherently incapable of removing some control parameters
    - water quality limitations not met in geographic area
- B. Need to reduce cost
    - rising sludge disposal costs
    - expensive chemicals used to aid biological treatment
- C. Need to expand treatment plant
    - want to accept new customers
    - currently overloaded
    - want to accept new product's wastewater; afraid biological process will become unstable or incapable of removing new waste constituents
    - can no longer use off plant sludge disposal site
- D. This treatment plant will eventually be abandoned (i. e., to join regional plant) but I have to get the most out of what I have

II New (potentially biological) Treatment Plants

- A. Want cost effective process
- B. Concern about efficiency of biological treatment
    - have potentially toxic waste
    - face strict effluent limits
    - want stable process
    - have wastewater from changing product line
    - future regulations might outdate biological treatment capabilities
- C. Have components in waste not currently regulated, but want them removed now.
- D. Limited amount of land available for treatment
- E. Want to minimize sludge disposal problems
    - have undesirable components in waste that will be concentrated in sludge; don't want these released to environment
    - don't have land, or availability of ocean disposal

III New Advanced Waste Treatment Plants

- A. Want cost effective process
- B. Want flexibility to alter treatment plant
    - as regulations change
    - as product mix dictates different treatment need -
        - over short intervals
        - over a long period
- C. Concerned about stability of alternate advanced treatment processes

    D. Want to minimize investment

IV Miscellaneous

    A. Pretreatment plus municipal disposal route too expensive

    B. PACT is a low risk process compatible with many existing waste processing schemes, changes in product mix, or changes in regulations

TABLE III - ECONOMIC CONSIDERATIONS OF POWDERED ACTIVATED CARBON ADDITION

PRO	CON
● Eliminates granular carbon adsorption equipment needs, including initial GAC inventory	● Powdered Carbon Cost - virgin about 0.5-0.8¢/1000 liters/10ppm using 55 to 80¢/kg carbon
	● Regenerated (full cost) - about 0.1-0.2¢/1000 liters/10ppm
● Minimizes need for equalization facilities to control wastewater variability	
● Eliminates separate secondary sludge disposal if regeneration is used	
● Reduces or eliminates need for antifoam, odor control	● May require use of flocculant
● Protects biological system from inhibition or toxic upset	
● Reduces size requirements for secondary sludge settling, thickening, dewatering	
● Carbon addition rate readily changed for changes in wastewater characteristics or regulations	

TABLE IV - CHAMBERS WORKS HALF FULL FLOWRATE TEST
TEST PERIOD 3/13/77-3/26/77 INCLUSIVE

		BENCH SCALE CONTROLS	
	FULL SCALE PACT PLANT	PACT	CONVENTIONAL BIOLOGICAL
Operating Conditions			
Carbon Dose(ppm)	182	150	0
Aeration Temp (°C)	22	22	22
Hydraulic Residence Time (hrs)	14.6	7.5	7.5
Sludge Age (days)	*	8	8
Feed Quality			
BOD-Soluble (mg/l)	304	304	304
DOC (mg/l)	214	214	214
Color (APHA)	1416	1416	1416
Effluent Quality			
BOD-Soluble (mg/l)	15.2	19.3	13.8
DOC (mg/l)	35.7	28.4	67.3
Color (APHA)	311	369	1900

*no steady state material balance available

TABLE V - CHAMBERS WORKS FULL FLOWRATE TEST
TEST PERIOD 4/26/77-5/6/77 INCLUSIVE

Operating Conditions	
Carbon Dose (ppm)	189
Aeration Temp (°C)	28.5
Hydraulic Residence Time (hrs)	7.5
Feed Quality	
BOD - Soluble (mg/l)	300
DOC - (mg/l)	214
Color (APHA)	2080
Effluent Quality	
BOD - Soluble (mg/l)	9.6
DOC - (mg/l)	28
Color (APHA)	490

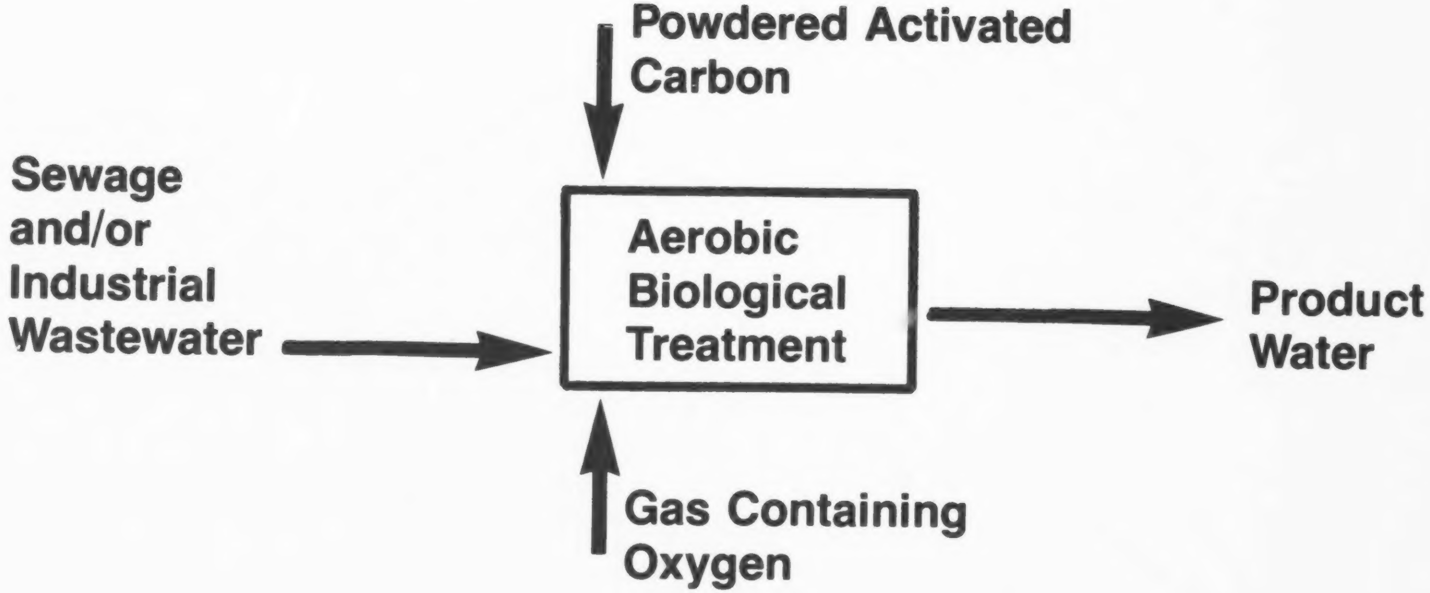
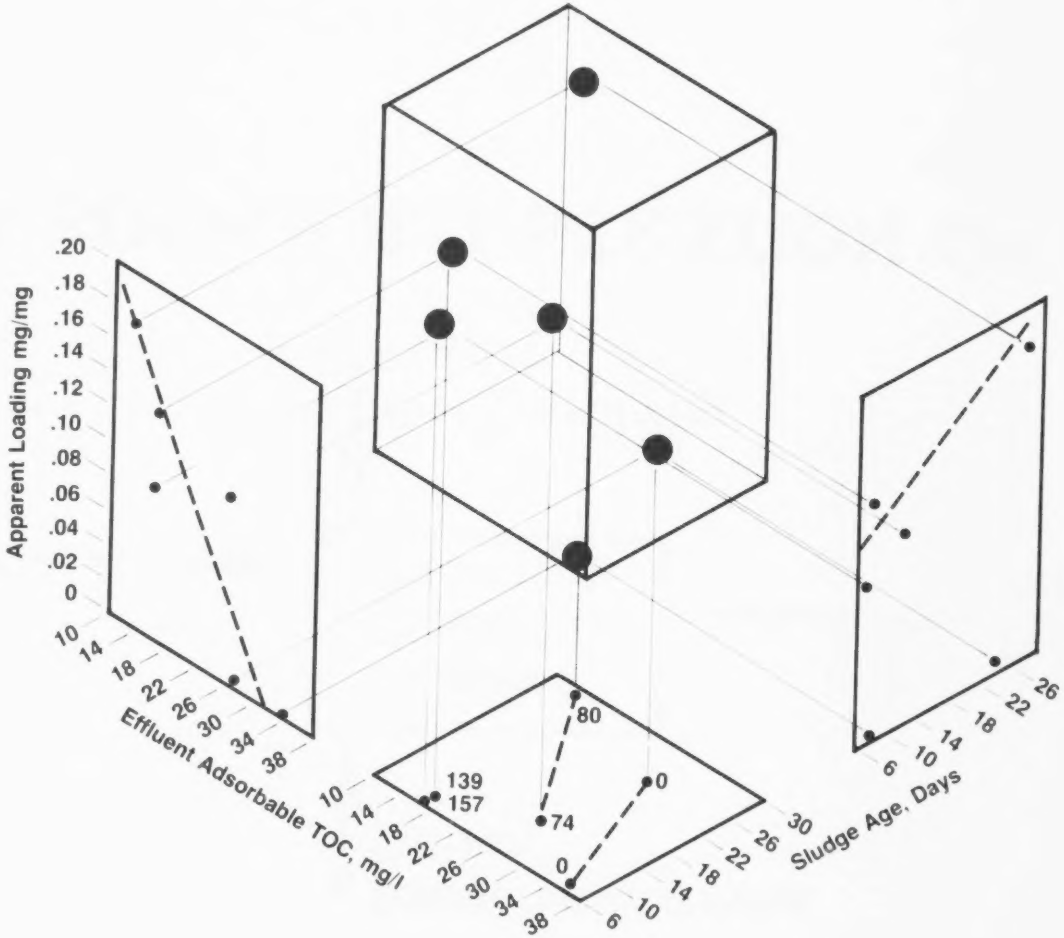
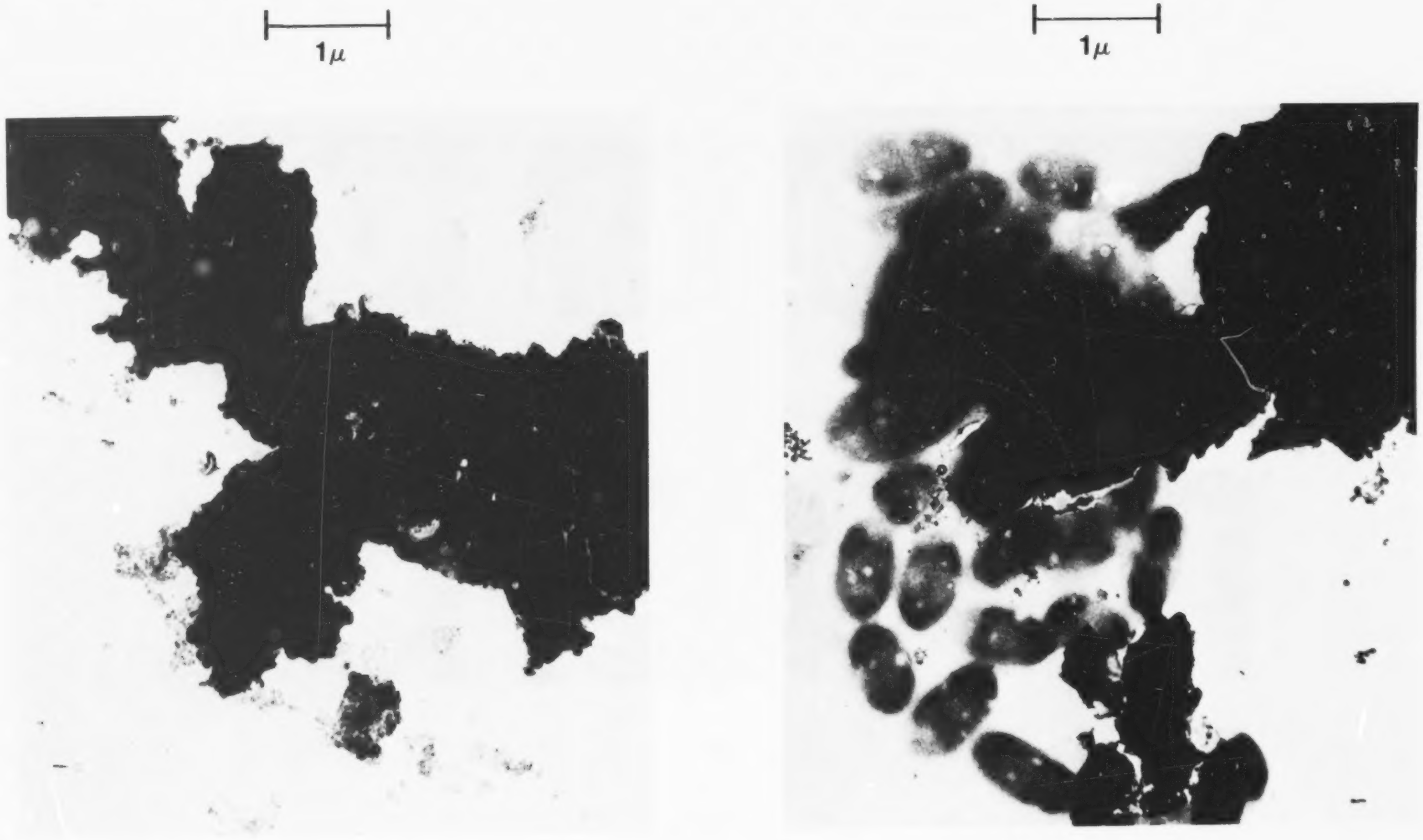

Powdered Activated
Carbon
Sewage
and/or
Industrial
Wastewater
Aerobic
Biological
Treatment
Product
Water
Gas Containing
Oxygen

Fig. 1 A SIMPLE ILLUSTRATION OF PACT



*Numbers shown in the bottom face of the exploded cube are applied carbon doses, mg/liter

Fig. 2 EFFECT OF SLUDGE AGE AND CARBON DOSE ON EFFLUENT TOC AND APPARENT LOADING



Left:

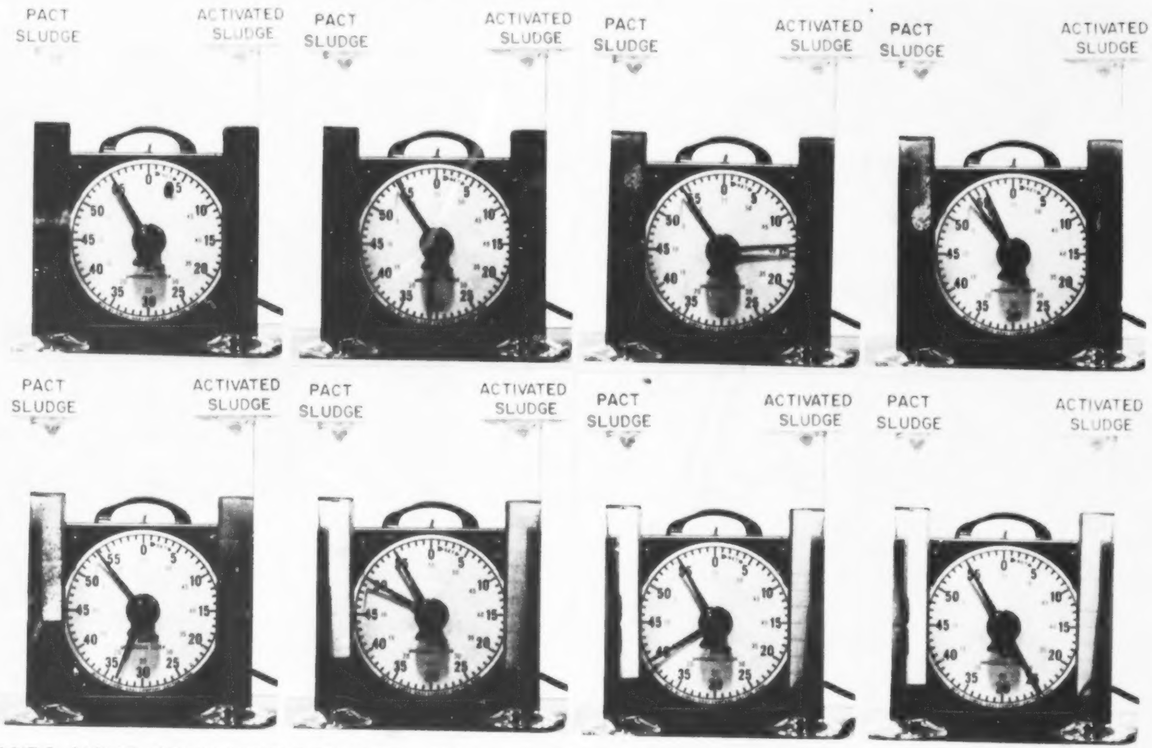
Virgin Carbon in Water

Right:

PACT Sludge

Fig. 3 PHOTOMICROGRAPHS

	INTIAL SOLIDS, MG/L	SLUDGE VOLUME INDEX, CC/GRAM
PACT	7708 ± 896	20 ± 2
ACTIVATED SLUDGE	2412 ± 150	46 ± 3


PACT SLUDGE
ACTIVATED SLUDGE
PACT SLUDGE
ACTIVATED SLUDGE
PACT SLUDGE
ACTIVATED SLUDGE
PACT SLUDGE
ACTIVATED SLUDGE
PACT SLUDGE
ACTIVATED SLUDGE
PACT SLUDGE
ACTIVATED SLUDGE
PACT SLUDGE
ACTIVATED SLUDGE
PACT SLUDGE
ACTIVATED SLUDGE

NOTE: TIMER HANDS MOVE COUNTERCLOCKWISE. READ ELAPSED TIME USING SMALL NUMBERS.
LONG HAND INDICATES MINUTES, SHORT HAND INDICATES SECONDS.
FOR EXAMPLE, LOWER LEFT TIMER READS 1 MINUTE, 21 SECONDS.
BOTH SLUDGES FROM TREATABILITY UNITS AT SAME SLUDGEAGE, HYDRAULIC DETENTION TIME.

Fig.4 COMPARATIVE SETTLING CHARACTERISTICS OF PACT AND ACTIVATED SLUDGE

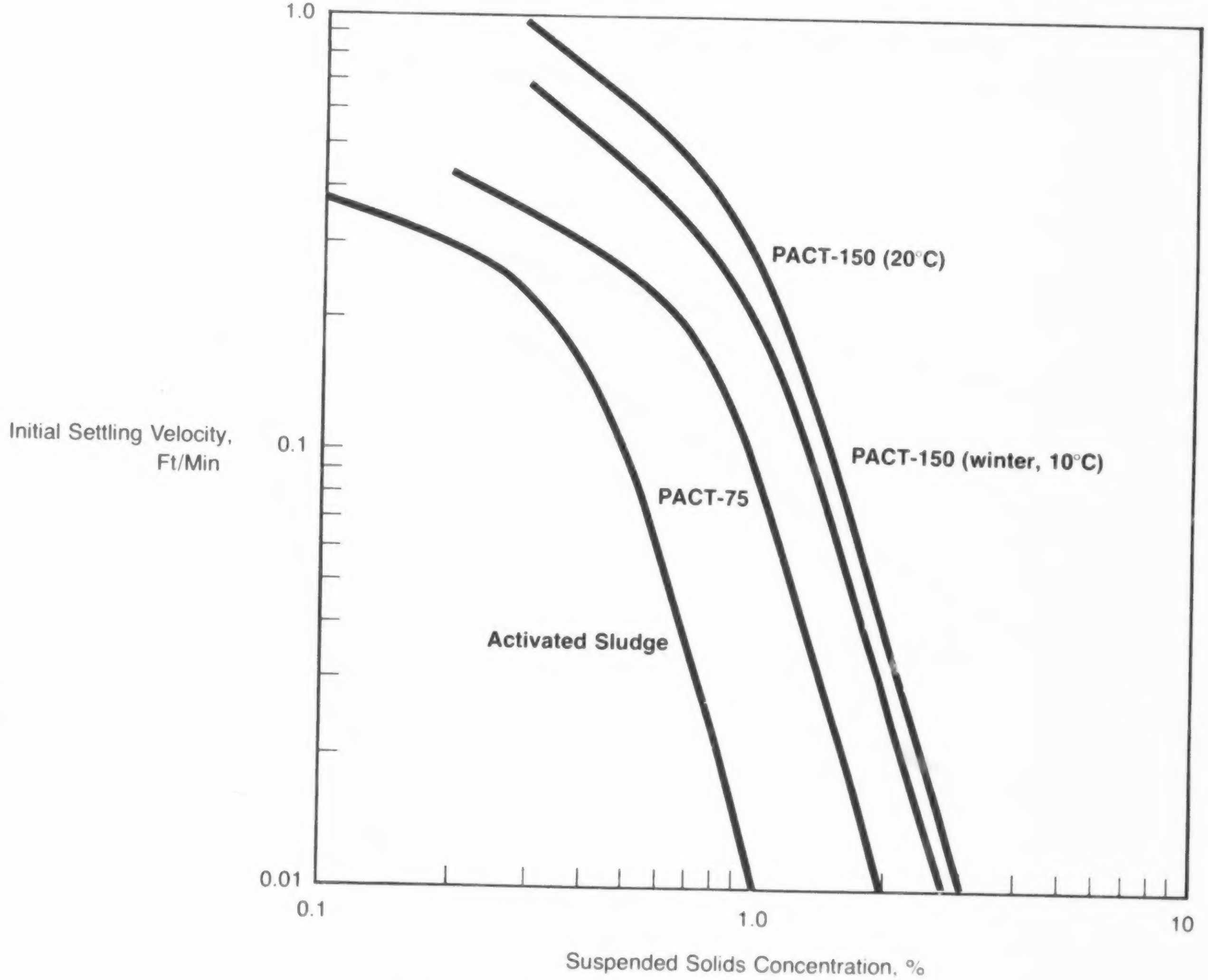


Fig. 5 SETTLING CHARACTERISTICS OF PACT & ACTIVATED SLUDGES

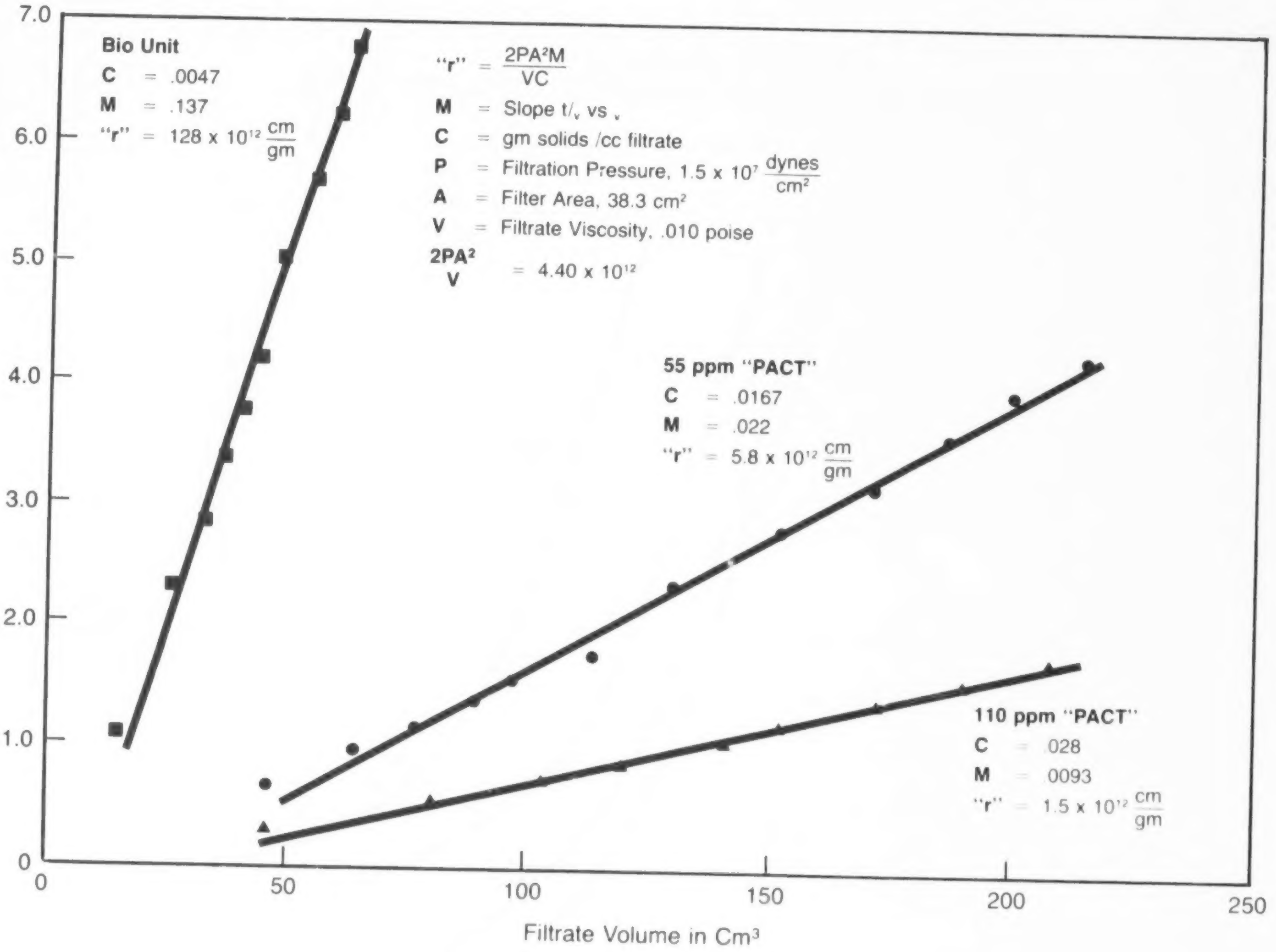


Fig. 6 SPECIFIC RESISTANCE, "r" OF PACT vs BIOLOGICAL SLUDGE

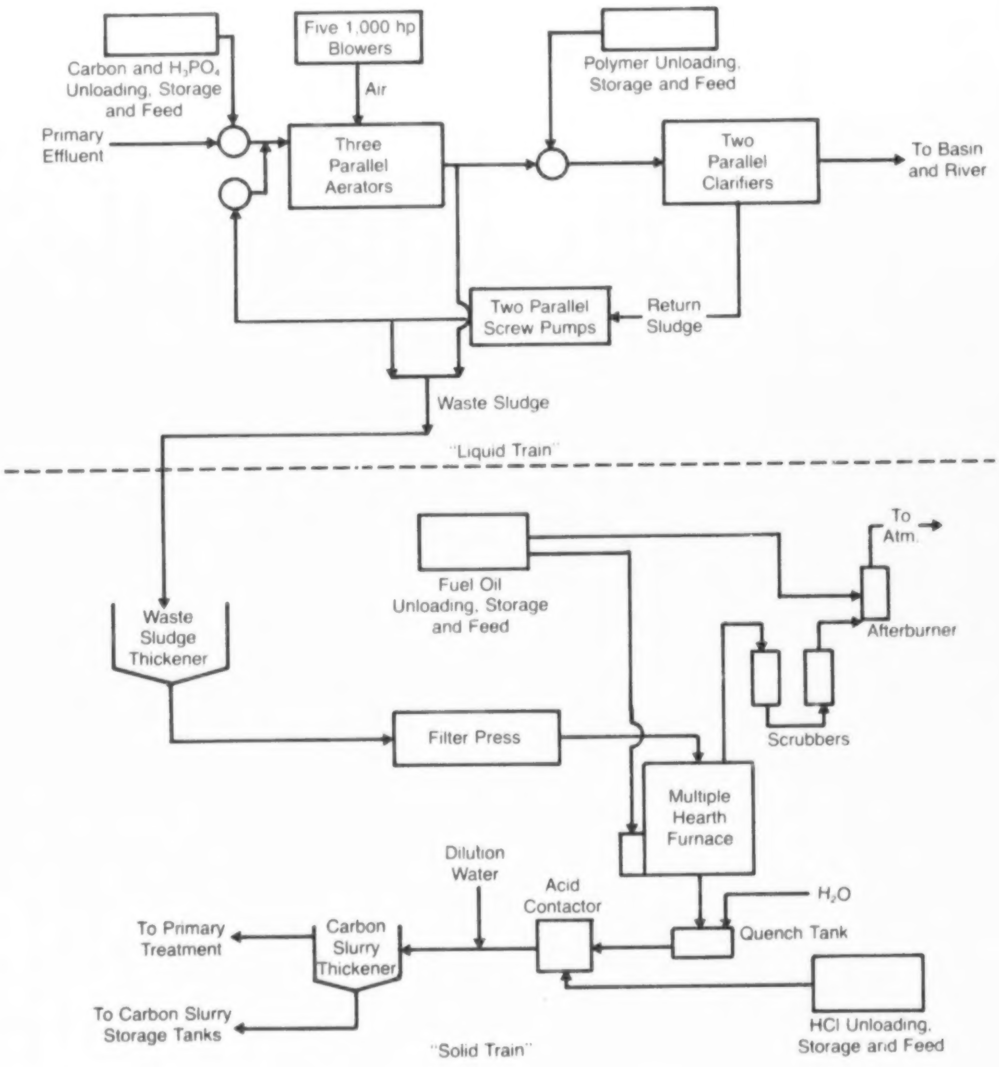

Carbon and H_3PO_4 Unloading, Storage and Feed
Five 1,000 hp Blowers
Air
Polymer Unloading, Storage and Feed
Primary Effluent
Three Parallel Aerators
Two Parallel Clarifiers
To Basin and River
Two Parallel Screw Pumps
Return Sludge
Waste Sludge
"Liquid Train"
Fuel Oil Unloading, Storage and Feed
To Atm.
Afterburner
Waste Sludge Thickener
Scrubbers
Filter Press
Multiple Hearth Furnace
Dilution Water
Acid Contactor
H_2O
Quench Tank
To Primary Treatment
Carbon Slurry Thickener
To Carbon Slurry Storage Tanks
"Solid Train"
HCl Unloading, Storage and Feed

Fig. 7 DU PONT PACT PROCESS: CHAMBERS WORKS

POWDERED ACTIVATED CARBON ENHANCEMENT OF ACTIVATED SLUDGE FOR BATEA REFINERY WASTEWATER TREATMENT

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Project Director, Standard Oil Company (Indiana)

James F. Grutsch
Coordinator of Environmental Projects, Standard Oil Company (Indiana)

ABSTRACT

Pilot plant studies show that powdered activated carbon enhancement of activated sludge is a viable alternate to and less costly substitute for granular carbon tertiary treatment of refinery wastewaters. Effluent quality depends upon both the equilibrium concentration and the surface area of the powdered carbon in the activated sludge mixed-liquor.

Operation at very high sludge ages--60 days or more--allows the carbon to accumulate to high concentrations in the mixed-liquor even though only small make-up amounts are added to the system. Also, carbons with a high surface area are especially efficient in adsorbing contaminants. Consequently, costly regeneration may be unnecessary because the spent carbon can simply be discarded with the waste sludge. Powdered carbons may thus eliminate the need for the add-on granular carbon adsorption process that the Environmental Protection Agency has recommended for meeting proposed 1983 standards for Best Available Technology Economically Achievable (BATEA).

INTRODUCTION

According to the EPA guidelines for treating refinery wastewaters[1#], the sequence shown in Figure 1 is recommended for meeting 1977 standards for Best Practical Technology Currently Available (BPTCA). For meeting 1983 goals for Best Available Technology Economically Achievable (BATEA), the guidelines recommend an add-on process using granular carbon adsorption. However, this approach may be both inefficient and very costly. So far as is known, its effectiveness has never been adequately demonstrated. Moreover, preliminary estimates indicate that capital and operating costs for the granular carbon adsorption and regeneration facilities may equal or exceed those of the entire current activated sludge process.

By contrast, both patents and research studies[2-25] indicate that powdered activated carbon may be a practical and economical substitute for granular carbon. For example, powdered carbon costs only about one-half as much as

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[#] References inserted at end of text.

granular--$0.65/kg versus $1.20/kg[15]. In addition, recent studies have shown that powdered carbon can be added directly to the mixed-liquor in activated sludge aeration tanks [21, 22, 23, 24]. Thus, appropriate alterations in operating procedures may eliminate the need for regeneration by making it economically feasible to discard the spent carbon with the waste sludge.

In general, the cost effectiveness of a powdered carbon process increases with the concentration of carbon maintained in the mixed-liquor. A mass balance of such a process is represented by the following equation:

$$C = \frac{C_i \ \theta_c}{\theta_h} \qquad (1)$$

where

C = Equilibrium mixed-liquor carbon concentration (mg/l)
C_i = Influent carbon concentration (mg/l)
θ_c = Sludge age (days)
θ_h = Hydraulic retention time in the aeration tank (days)

Equation 1 reveals that the equilibrium mixed-liquor carbon concentration is proportional to the product of the influent carbon concentration (carbon dose) and the sludge age. Thus, equilibrium carbon concentration can be increased by increasing the carbon dose, or the sludge age, or both. Therefore, to keep carbon costs to a minimum, it is desirable to operate at as high a sludge age as possible and not at an excessively long hydraulic retention time.

A possible drawback to operation at a high sludge age is the increased risk that toxic, inhibitory, or inert materials will build up in the aeration tank. For example, a build-up of oily solids could reduce the oxygen transfer efficiency and inhibit both the nitrifying and organic carbon utilizing organisms. The dissolved oxygen concentration in the mixed-liquor could also become too low for effective nitrification, and the final clarifiers could become overloaded. Therefore, it is desirable in the pretreatment step to remove as much solid material as possible from the wastewater before it enters the aeration tank.

To evaluate the effects of such variables in a process using powdered carbon, an extensive 15 month four-phase pilot plant study was carried out at Amoco Oil Company's Texas City refinery. Pilot plants operating in parallel with the refinery activated sludge process facility were fed the same wastewater for treatment. Specific variables investigated were:

Carbon type, including surface area and pore volume

Carbon addition rate

Sludge Age

Pretreatment of feed to remove oil and solids

EXPERIMENTAL EQUIPMENT

Figure 2 shows the configuration of the pilot plants. Each had a volume of 42 liters, and as many as eight units were operated in parallel during portions of the study. They were housed in a rain-tight enclosure but were neither heated nor cooled. Thus, the temperature of the mixed-liquor varied from 4°C to 31°C.

Operating conditions and analytical procedures are summarized in Table 1. The pH was checked daily and controlled by addition of caustic at a constant rate. Dibasic potassium phosphate, K_2HPO_4, was added to satisy the phosphorus requirement of the microorganisms.

The wastewater feed, a slipstream from the pressure filters of the refinery treatment plant, was passed through a pilot gravity sand filter before being fed to the pilot plants.

Table 2 summarizes the characteristics of the five powdered carbons evaluated. Amoco's experimental high-surface-area carbons are designated as A1 and A2, PX-21 and PX-23, respectively. Those designated as B, C, and D are commercially available carbons having a much lower surface area. Carbon A2 (PX-23) has the highest pore volume.

Effectiveness was judged on the basis of the following effluent standards proposed for a BATEA facility[1]:

	Concentration, mg/liter
Total Organic Carbon (TOC)	15
Chemical Oxygen Demand (COD)	24
Ammonia (NH_3-N)	6.3
Phenolics	0.02

These standards are for a Class "C" refinery and are based on the guideline effluent flow rate of 0.46 m^3/m^3 of crude throughput per stream day (19 gal/bbl). Because the BATEA treatment sequence will undoubtedly result in very low concentrations of effluent suspended solids, only the soluble components of the effluent were measured.

To obtain high sludge ages, effluent suspended solids were allowed to settle in 30-gallon plastic containers and then were returned to the pilot plants periodically. At any given sludge age, all plants were allowed to reach steady-state operation over an extended period of time. Then performance data were taken over a 30-day period.

RESULTS AND DISCUSSION

The four phases of the study were carried out in sequence, with the design of succeeding phases based on the results of the preceding ones. In summary, they examined:

Phase	Objective
I	Effect of carbon type at an addition rate of 100 mg/liter and a sludge age of 20 days with prefiltered feed.
II	Effect of carbon type at an addition rate of 200 mg/liter and a sludge age of 20 days with prefiltered feed.
III	Effect of increasing sludge age to 60 days and reducing carbon addition rate to 25 mg/liter with unfiltered and prefiltered feed.
IV	Effect of further increasing sludge age to 150 days while reducing carbon addition rate to 10 mg/liter.

Phases I and II

The results of Phases I and II, summarized in Table 3, indicate that powdered activated carbon significantly enhances the performance of a refinery activated sludge process. Improvement in the quality of the effluents from carbon-fed plants ranged from 65% for soluble organic carbon up to 95% for phenolics. At the 200 mg/liter addition rate, the results usually satisfied the BATEA effluent quality goals. The high surface area carbon A1 was significantly more effective than the other three. The commercially available carbon B produced slightly better effluent than carbon C, which would be expected if efficiency is proportional to surface area. Because nitrification was essentially complete in the control unit, carbon addition could not improve ammonia conversion. Carbon D, which is derived from wood charcoal and has a significantly lower pore volume than the others, performed so poorly in Phase I that it was dropped from further consideration. The performance of carbon A1 at 100 mg/liter dose was about as effective as carbon B at 200 mg/liter, or about twice as effective as the best commercially available carbon tested.

Phase III

Table 4 shows the effects of sludge age and feed filtration upon performance. The plant with filtered feed performed better than one with unfiltered feed, and a sludge age of 60 days was better than one of 20 days. No deterioration in the settling characteristics of the mixed-liquor suspended solids was observed at this higher sludge age.

At a sludge age of 20 days the plant with filtered feed performed marginally better than the one with unfiltered feed. Undoubtedly, greater differences in effluent quality would have been observed in a plant operated at a sludge age of 60 days with unfiltered feed. (Not recorded in these data, however, is the complete failure of the plant fed unfiltered feed shortly after cessation of data gathering for this steady-state period.)

Table 4 also shows how pore size and surface area affect the performance of the carbons. Carbons A1 and A2 have approximately the same surface area, but carbon A2 has much larger pores. Yet, at an equivalent addition rate of 50 mg/liter, both carbons showed about the same performance. Thus, large pore diameters are not required for effective treatment of this refinery wastewater. Moreover, plants fed 50 mg/liter of either A1 or A2 performed much better than the plant fed 100 mg/liter of carbon B. In fact, these high-surface-area carbons are between two and four times more effective than carbon B in enhancing SOC and soluble COD removal.

A comparison of the data in Tables 3 and 4 shows that a low carbon dose and a high sludge age enhance an activated sludge process almost as much as do a high carbon dose and a low sludge age.

It is possible that the difference in performance is solely due to difference in temperature between the phases--mean operating temperature during Phase III was only 14°C, whereas during Phases I and II temperature averaged 31°C and 25°C, respectively.

Also observed during the lower operating temperature of Phase III was an increase in the ammonia removal efficiency of the carbon-fed pilot plants. This phenomenon was unexpected because activated carbon does not normally adsorb ammonia. Possibly, the increased removal rate is due to the adsorption of potentially toxic or inhibitory organic materials which would reduce the rate of nitrification if left in solution. The control plant in Phases I and II had little difficulty in achieving full nitrification, perhaps because of the higher temperature.

Phase IV

As shown in Table 5, Phase IV was designed to push the activated sludge system to the limit by increasing sludge age to 150 days and decreasing carbon addition to 10 mg/liter. Further, in one of the plants, hydraulic retention time was reduced to 7.5 hours, compared with 15 hours in the other plants.

Despite similarities in influent quality during all four phases, during Phase IV the effluent SOC and COD of the control increased by about 30-35% over that observed during the first three phases, despite a mean temperature of 27°C (c.f. 14°C during Phase III). All pilot plants essentially nitrified completely.

Remarkably, however, the plant with 10 mg/liter of high surface area carbon A1 at a sludge age of 150 days produced an effluent whose soluble organic carbon concentration was 50% lower than that of the control reactor and slightly lower than that of all of the other pilot plants. The plant dosed with 25 mg/liter carbon A1, with one-half the hydraulic capacity of the other plants, produced the second best effluent.

The outstanding performance at a sludge age of 150 days indicates that refinery activated sludge processes can be operated with very little added carbon. The dose may be low enough so that the carbon need not be regenerated but be discarded with the waste activated sludge. At a very high sludge age, there will be smaller quantities of waste sludge to be disposed of.

The data in Table 5 also indicates that powdered carbon can be used to increase the hydraulic capacity of an activated sludge plant, as proposed by others[13], or to increase the effluent quality of an overloaded plant. The carbon-fed plant that operated at one-half the hydraulic retention time of the control produced an effluent 50% better than that of the control. Experience with pilot activated sludge plants operated at several of Amoco's other refineries has shown that conventional activated sludge processes cannot be operated successfully with a hydraulic residence time of only 7½ hours.

Status of Powdered Carbon Enhancement of Activated Sludge

The data from Phase IV indicate that the limits of the powdered carbon enhanced activated sludge process have not been reached. In addition, more data are needed before economic studies can be made to weigh the possible options for achieving a given effluent quality: high fresh carbon dose at moderate sludge age (20-60 days) with regeneration of spent carbon; low fresh carbon dose at high sludge age (60-150 days) with no regeneration of spent carbon. Cost analyses should be made for each of these extreme options, and several intermediate ones, and compared with those for tertiary treatment with granular carbon technology.

Figure 3 shows the qualitative curves this pilot study has generated. Of course, the one for the 150-day sludge age is purely speculative because only one data point exists. However, the trend of the data does show that effluent quality is a function of mixed-liquor carbon concentration. The curves are probably asymptotic to a residual organic carbon concentration, but over the range investigated an increase in mixed-liquor carbon concentration causes a decrease in effluent soluble organic carbon. Furthermore, the relationship between effluent quality, sludge age, and carbon dose is clearly non-linear. For example, to achieve an effluent quality of 12.5 mg/liter of soluble organic carbon, the three options are: 100 mg/liter of carbon at a sludge age of 20 days; 47 mg/liter of carbon at a sludge age of 60 days; 24 mg/liter of carbon at a sludge age of 150 days. If the relationship were linear, the values calculated from a base case of 100 mg/liter at a 20-day sludge age would be 33 mg/liter and 13 mg/liter at 60 days and 150 days, respectively.

Apparently, the process loses effectiveness because of incomplete microbial regeneration. Microbial regeneration of the spent carbon is probably not as effective as using fresh carbon; some materials adsorbed by the carbon are undoubtedly non-biodegradable, even after 150 days of contact with microorganisms in the pilot plant. The ability to retain significant effectiveness even at 150 days is the key to cost effective high sludge age operation with powdered activated carbon. Of course, there may be other reasons why carbon loses effectiveness at high sludge age, such as production of cell lysis products which are then adsorbed by the carbon.

Effluent Variability

Variation in effluent quality over a 30-day (or longer) period is extremely important. The EPA[1] has set the daily maximum variability equivalent to the 99% probability value and the 30-day maximum variability to the 98% level. For BATEA the daily maximum variability factors for TOC, COD, NH_3-N, and phenolics are proposed at 1.6, 2.0, 2.0, and 2.4, respectively. The 30-day maximum values are 1.3, 1.6, 1.5, and 1.7, respectively.

Figures 4, 5, 6, and 7 show probability data for the 30-day operating periods during Phase III. Table 6 shows the daily maximum (99% probability) and 30-day maximum (98% probability) variability factors calculated from these figures for the plant fed with 25 mg/liter of Carbon A1. The EPA guideline values are also given. The actual variability factor was calculated as the 99% (or 98%) probability value divided by the target quality value. In general, the variability in effluent quality was higher than the guideline values.

It is important to note that the proposed guideline variability factors are unrealistic. The data base used by EPA[1] for their production was obtained from limited pilot studies. In addition, BPTCA 30-day maximum (98% probability) values were used as the BATEA 30-day maximum values. Variability factors will undoubtedly have to be amended before BATEA goals become BATEA standards.

SUMMARY AND CONCLUSIONS

A viable alternative to granular activated carbon tertiary treatment of refinery activated sludge effluent for meeting proposed 1983 BATEA effluent quality standards has been demonstrated. The proposed process involves adding powdered activated carbon to the aeration tank of the activated sludge process, achieving cost effectiveness by operating at a very high sludge age and a low carbon dose. Effective removal of oil and colloidal solids in the pretreatment step is necessary for successful operation.

Effluent quality depends upon both the equilibrium mixed-liquor carbon concentration and the surface area of the carbon. An experimental carbon with a high surface area appears to be several times more effective than the best commercial carbons in achieving an effluent quality standard. Pore size of the activated carbon had no apparent effect upon effluent quality.

In general, the process can be used to meet only the long-term average effluent quality proposed for BATEA. Daily maximum and 30-day maximum variability goals, as presently defined cannot be met.

The proposed process also enhances nitrification at low temperatures and dampens effects of increased hydraulic flow rate on the activated sludge factors. Both phenomena will help to decrease effluent variability.

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DISCUSSION

Piysuch Shah, Exxon Research and Engineering Co.: Would you please comment on the effects of toxicant build up and on the performance of aged activated sludge units, especially 100-150 days? Also, what is the maximum concentration that can be allowed in the feed?

Grieves: Assume a very high sludge age of 150 days, a hydraulic residence time of 12 hours, 1 mg/liter of a toxicant (for example, chromium) in the feed, and 100% removal of it by the activated sludge. At steady state, chromium concentration would build up to 300 mg/liter, which, in all likelihood, would be toxic to the microorganisms. However, we have data to indicate that even at 150 days sludge age, chromium does not accumulate to more than 30-50 mg/liter in the sludge. We certainly have not observed any effects of toxicant build-up -- on the contrary, the 150-day sludge age reactor is the most effective unit.

As for other toxicants -- for example oil and grease and inert suspended solids -- if they are not effectively removed by prefiltration, or air flotation, they could very well accumulate to toxic or inhibitory concentrations in the mixed-liquor. As well as being toxic or inhibitory to microorganisms, especially nitrifiers, oxygen transfer problems will be encountered. High inert solids concentrations may also cause overloading problems in the final clarifier.

Ed Sebesta, Brown & Root, Inc.: The data indicates that nitrification occurred during some phases of the experiments while nitrification did not occur during other phases. Do you have any comments about why this occurred?

Grieves: If you have ever operated a refinery wastewater treatment facility, you will know that frequently there are excursions with nitrification. We achieved good nitrification during the warm operating periods, phases I and II. During phase III operation, it was relatively cool -- we recorded a mixed-liquor temperature of 2°C on one occasion, quite a severe winter for this part of Texas -- and, as expected, nitrification in the control activated sludge plant was poor. This is reflected in the probability plot (Figure 6) of the data. However, in the activated sludge pilot plants to which carbon was added, almost complete nitrification was observed. This was unexpected because, as you know, carbon does not normally adsorb ammonia.

Bob Smith, Carborundum Co.: Have you compared the cost effectiveness of the high capacity Amoco carbon vs. the lower capacity carbons?

Grieves: No, we have not made this comparison yet. We have not decided whether to go commercial with our carbon or not. However, if and when we do decide to commercialize our product, you can rest assured that it will be cost effective with other commercially available carbons.

BIOGRAPHIES

Colin G. Grieves is a Research Engineer in the Water Conservation group at Amoco Oil Company's Research and Development department in Naperville Illinois. He has M.S. and Ph.D. degrees in Environmental Systems Engineering from Clemson University, Clemson, South Carolina, and a B.Sc. degree in Civil Engineering from the University of Newcastle Upon Tyne, England. Previous employment was in the Public Health Engineering Division of Babtie Shaw & Morton, Consulting Civil and Structural Engineering in Glasgow, Scotland. Colin is the author of several papers in the wastewater treatment field.

Michael K. Stenstrom is a Research Engineer in the Water Conservation group at Amoco Oil Company's Research and Development department in Naperville, Illinois. He has a B.S. degree in Electrical Engineering and M.S. and Ph.D. degrees in Environmental Systems Engineering from Clemson University, Clemson, South Carolina. Mike is the author of several papers dealing with various aspects of municipal and industrial wastewater treatment.

BIOGRAPHIES

Joe D. Walk is Active Carbon Project Director in the Corporate Development Department of Standard Oil (Indiana), Chicago, Illinois. He has a B.S. degree in Chemical Engineering from the University of Texas. Previously he served as Process Coordinator in air/water conservation, crude running and product treating for Amoco Oil's ten refineries. Prior assignments include Manager of Technical department at Texas City refinery, as well as positions in New York City, New Orleans, and El Dorado, Arkansas, during his 31 years service with Standard Oil.

James F. Grutsch is Coordinator-Environmental Projects, Standard Oil Company (Indiana). He holds undergraduate and graduate degrees in chemistry from Indiana University. Prior to his present assignment with Standard, Jim served successfully as Group Leader for finishing, blending and reclamation at the Amoco Oil Whiting refinery, and Coordinator of Waste Disposal for Amoco. Jim taught undergraduate chemistry for 6 years at Indiana.

TABLE 1 OPERATING CONDITIONS

Pilot Plant Conditions

Aeration Zone Volume	36.7	liters
Settling Zone Volume	5.7	liters
Nominal Flow Rate	2.45	liters/hr.
Nominal Hydraulic Retention Time	15.0	hours
Nominal Settling Time	2.33	hours
Air Flow Rate	300	liters/hr.
pH	6-8.5	
Caustic Addition Rate	0.12-0.30	liters/hr.
Phosphorous Added to Feed	3	mg/liter
Temperature	Ambient (4-31°C)	

Analytical Work

Frequency	Analysis Performed[27, 28]
Daily	Influent and mixed-liquor pH, temperature, influent flow rate, caustic addition rate. Carbon addition and sludge wastage.
3 Times a Week	Influent and effluent total and volatile suspended solids, soluble organic carbon, soluble chemical oxygen demand, soluble ammonia nitrogen, and soluble phenolics. Mixed-liquor suspended solids and mixed-liquor volatile suspended solids. Sludge volume index.
Once a Week	Material balances to calculate quantity of sludge to be wasted to maintain desired sludge age.

TABLE 2 PROPERTIES OF POWDERED ACTIVATED CARBONS

Property	Carbon Designation				
	Experimental Amoco High Surface Area -		Commercially Available Conventional Surface Area Carbons		
	A1 Grade PX-21	A2 Grade PX-23	B	C	D
Surface Area					
BET, m^2/g	3099	3148	717	514	532
Pore Volume, cc/g					
> 15 A^o Radius	0.16	0.43	0.28	0.38	0.03
< 15 A^o Radius	1.45	1.60	0.51	0.11-0.42	0.25
Iodine Number	3349	3375	1790	920	888
Methylene Blue Adsorption, mg/g	586	550	100	83	50
Phenol Number	12.8	12.6	34.1	22.9	23.8
Bulk Density, g/cc	0.298	0.228	0.610	0.576	0.484
Screen Analysis					
Passes 100 Mesh, Wt.%	98.4	99.1	99.2	100.0	100.0
Passes 200 Mesh, Wt.%	92.7	93.4	86.7	94.4	97.9
Passes 325 Mesh, Wt.%	84.1	80.8	60.6	68.3	91.8
Molasses Number	10	205	103	85	0

TABLE 3

PHASES I AND II - EFFECT OF CARBON TYPE AND ADDITION RATE ON EFFLUENT QUALITY*
50% Probability Data During 30 Days of Steady-State Operation
Sludge Age = 20 Days

	Concentration, mg/liter					
		Pilot Plant Effluent				
Component	Filtered Influent	No Carbon	Carbon A1	Carbon B	Carbon C	Carbon D
Phase I: Carbon Addition Rate = 100 mg/liter Equil. Mixed-Liquor Temp = 31°C, Carbon Conc = 3200 mg/liter						
SOC	72.0	22.0	12.5	17.5	18.5	23.0
SCOD	230	73	28.5	48	44	65
NH_3-N	25.8	0.5	0.2	0.5	0.5	0.5
Phenolics	4.35	0.018	0.003	0.010	0.010	0.017
Phase II: Carbon Addition Rate = 200 mg/liter Equil. Mixed-Liquor Temp = 25°C, Carbon Conc = 6400 mg/liter						
SOC	70.0	26.5	9	13.5	15.5	
COD	230	58	17	24	28	
NH_3-N	25.4	0.2	0.2	0.2	0.1	
Phenolics	4.06	0.020	0.001	0.001	0.003	

* BATEA effluent standards in mg/liter are:

Soluble Organic Carbon (SOC)	15
Soluble COD (SCOD)	24
Ammonia Nitrogen (NH_3-N)	6.3
Phenolics	0.02

TABLE 4

PHASE III - EFFECT OF CARBON TYPE AND ADDITION RATE, SLUDGE AGE, AND INFLUENT PRETREATMENT ON EFFLUENT QUALITY

50% Probability Data During 30 Days of Steady-State Operation
Equil. Mixed-Liquor Temp = $14^{o}C$, Carbon Conc. = 2400 mg/liter

	Carbon		Influent Concentration, mg/liter			
Influent Pretreatment	Type	Addition Rate, mg/liter	SOC	COD	NH_3-N	Phenolics
Filtered Feed	-	-	73.5	294.5	19.3	3.95
			Effluent Concentration, mg/liter			
		Sludge Age = 20 Days				
Unfiltered	-	-	32.0	103.5	12.1	0.027
Filtered	-	-	29.0	83.0	14.5	0.027
		Sludge Age = 60 Days				
Filtered	-	-	25.0	65.9	5.1	0.019
Filtered	B	100	16.0	40.3	0.2	0.001
Filtered	A1	50	12.0	27.5	0.1	0.002
Filtered	A1	25	16.0	50.3	0.4	0.006
Filtered	A2	50	13.0	31.0	1.8	0.004

TABLE 5

PHASE IV - EFFECT OF HIGH SLUDGE AGE, LOW CARBON ADDITION RATE, AND DECREASED HYDRAULIC RETENTION TIME ON EFFLUENT QUALITY*
50% Probability Data During 30 Days of Steady-State Operation
Equil. Mixed-Liquor Temp = 27°C

Carbon					Effluent Conc, mg/liter			
Type	Addition Rate, mg/liter	Sludge Age, days	Hydraulic Retention Time, hr	Equil. Mixed Liquor Carbon Conc, mg/liter	SOC	COD	NH3-N	Phenolics
-	-	60	15	-	29	99	0.1	0.018
B	25	60	15	2400	22	64	0.1	0.010
Al	25	60	15	2400	18	52	0.1	0.010
Al	25	60	7.5	4800	17	46	0.3	0.010
Al	10	150	15	2400	16	49	0.1	0.010

* Filtered influent contained 78 mg/liter SOC, 270 mg/liter COD, 29 mg/liter NH_3-N, and 3.25 mg/liter phenolics.

TABLE 6

PHASE III - BAT GUIDELINE AND ACTUAL VARIABILITY FACTORS FOR PILOT PLANT FED 25 mg/liter OF CARBON A1

Parameter	BAT Guideline Variability Factor		Actual Variability Factor	
	Daily Max.	30 Day Max.	Daily Max.	30 Day Max.
Soluble Organic Carbon	1.6	1.3	2.8	2.8
Soluble COD	2.0	1.6	7.5	7.5
NH_3-N	2.0	1.5	2.1	2.0
Phenolics	2.4	1.7	5	5

FIGURE 1. SIMPLIFIED REFINERY BPT WASTEWATER TREATMENT SYSTEM

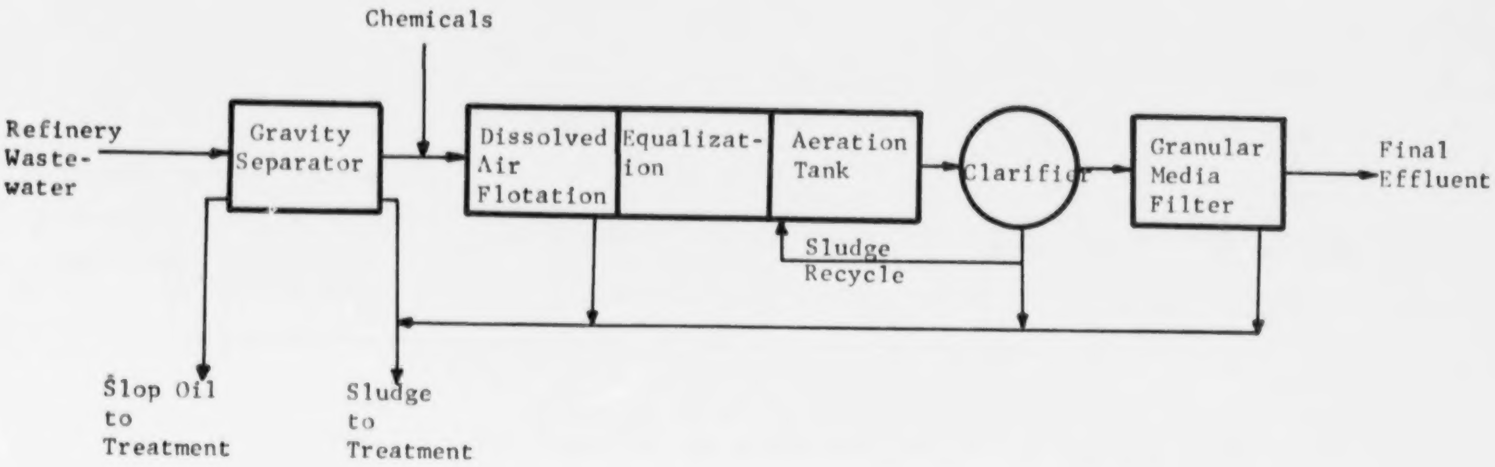

Chemicals
Refinery Waste-water
Gravity Separator
Dissolved Air Flotation
Equalization
Aeration Tank
Clarifier
Granular Media Filter
Final Effluent
Sludge Recycle
Slop Oil to Treatment
Sludge to Treatment

FIGURE 2. SCHEMATIC OF ACTIVATED SLUDGE REACTOR USED IN PILOT PROGRAM

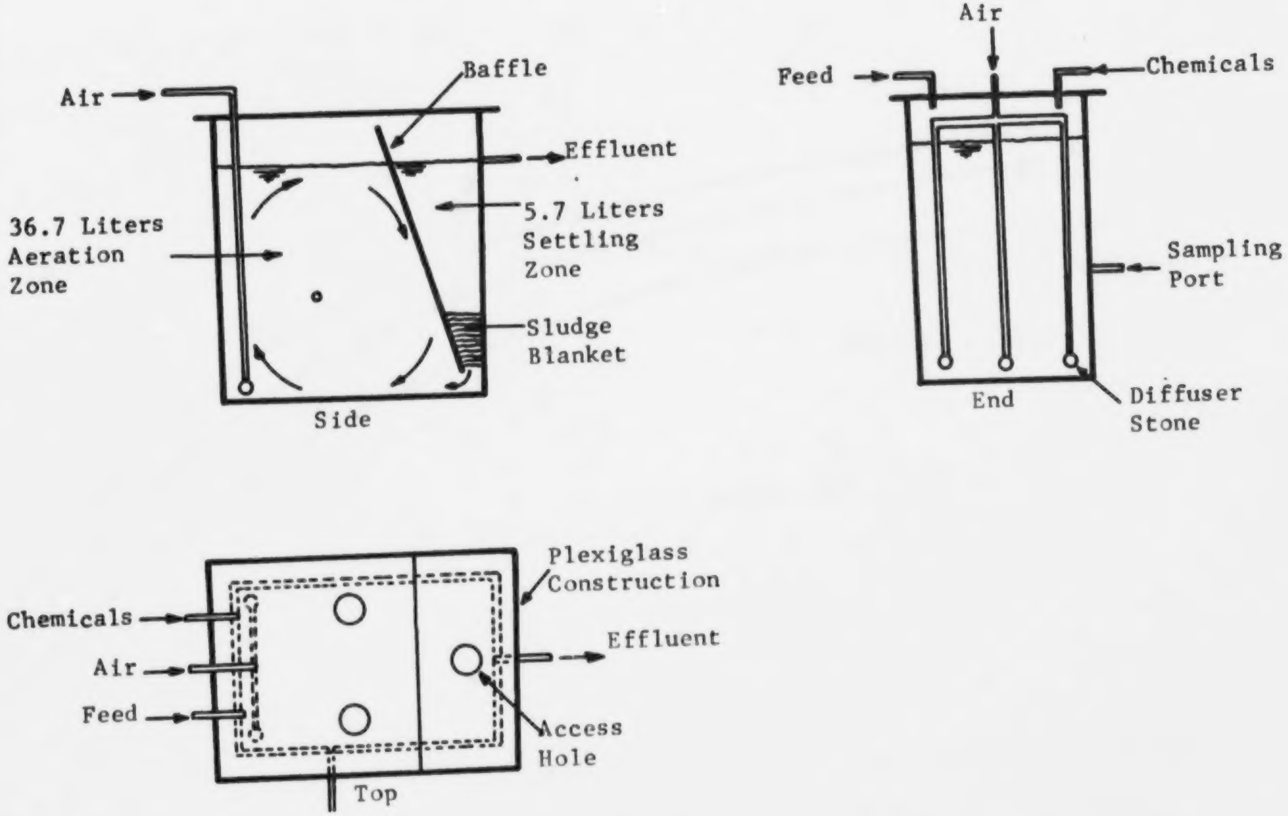

Air
Baffle
Effluent
36.7 Liters
Aeration
Zone
5.7 Liters
Settling
Zone
Sludge
Blanket
Side
Air
Feed
Chemicals
Sampling
Port
End
Diffuser
Stone
Plexiglass
Construction
Chemicals
Air
Feed
Effluent
Access
Hole
Top

FIGURE 3. EFFECT OF MIXED-LIQUOR CARBON CONCENTRATION ON EFFLUENT SOC

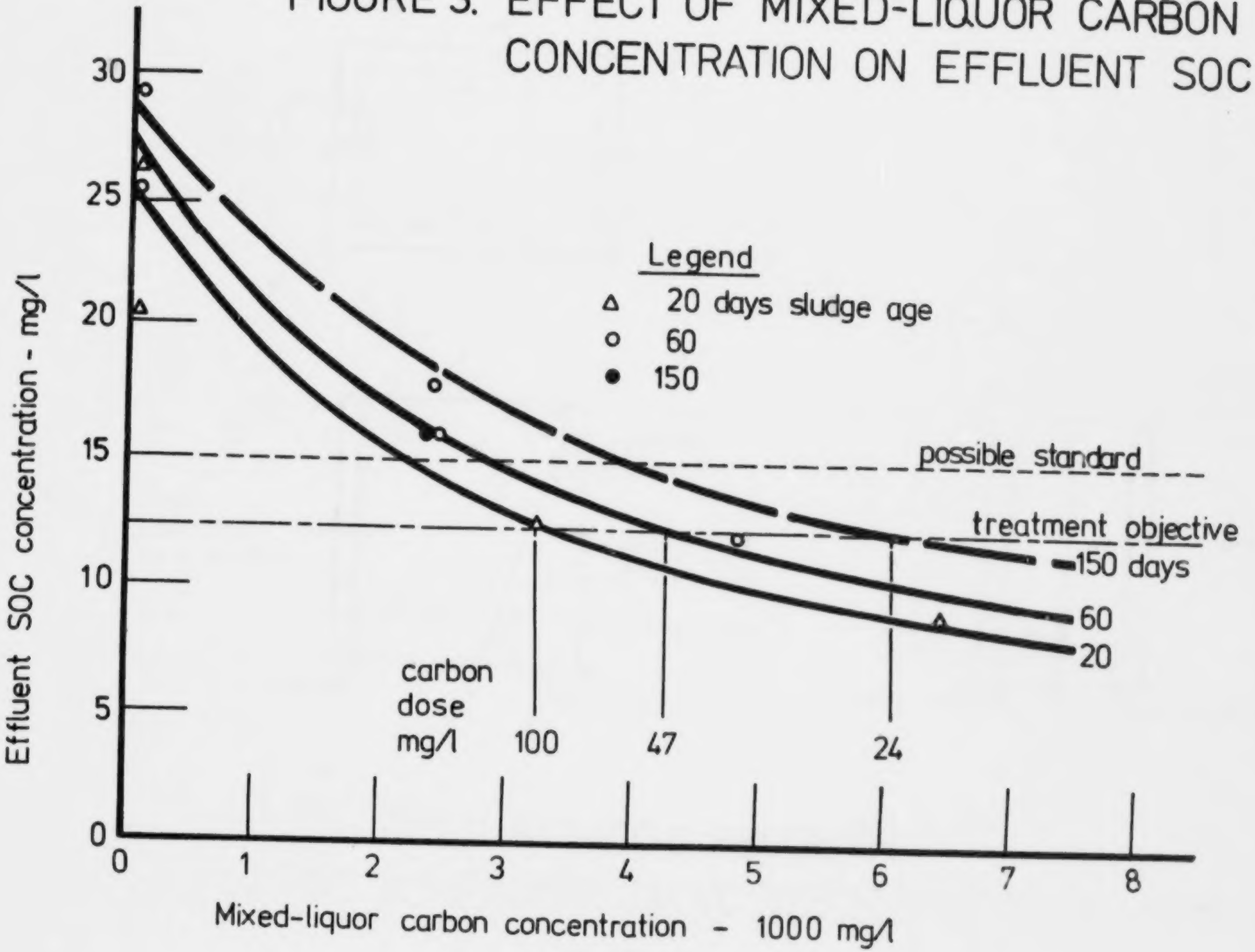


FIGURE 4 - SOLUBLE ORGANIC CARBON - PHASE 3

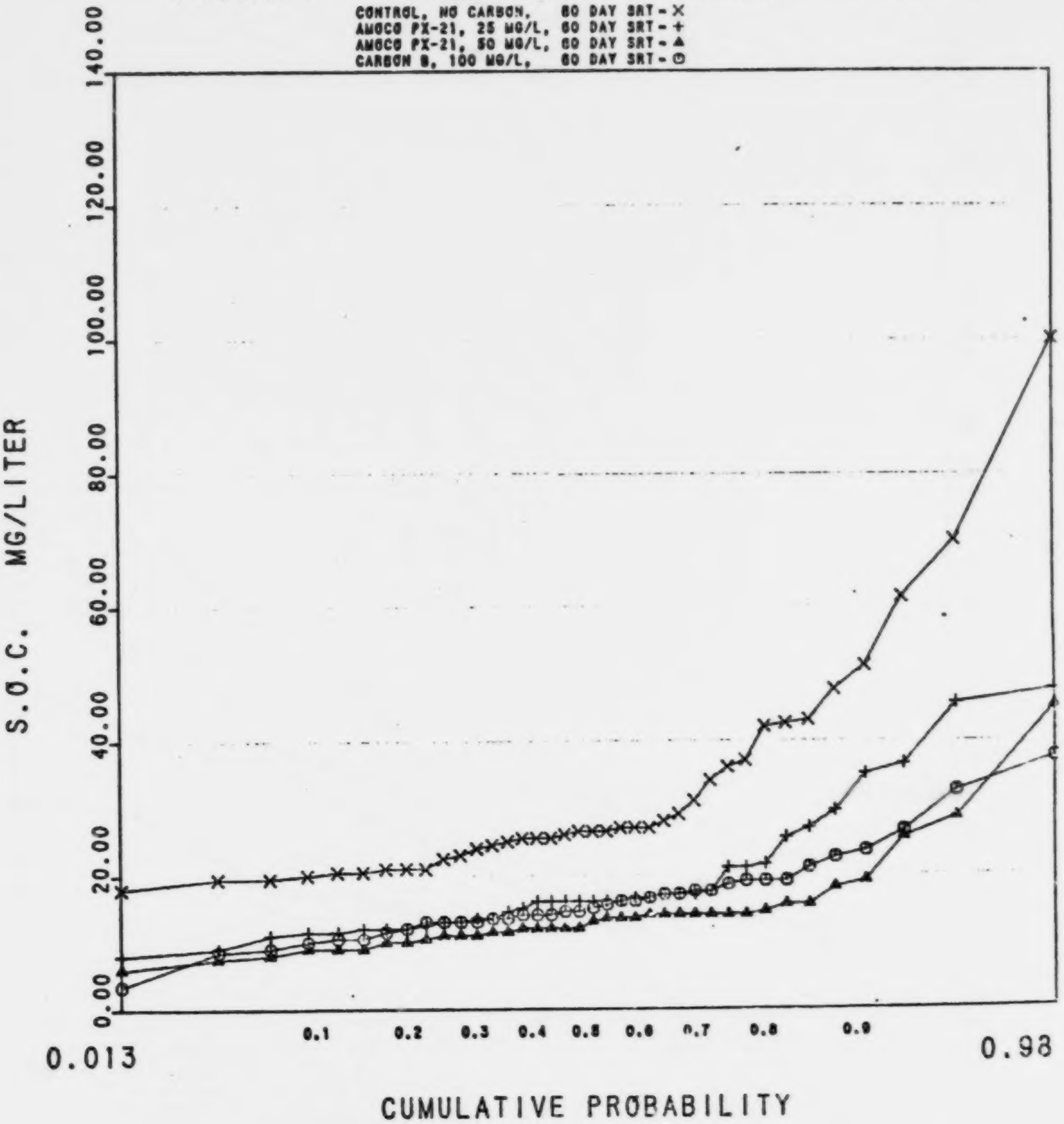


FIGURE 5 - SOLUBLE CHEMICAL OXYGEN DEMAND

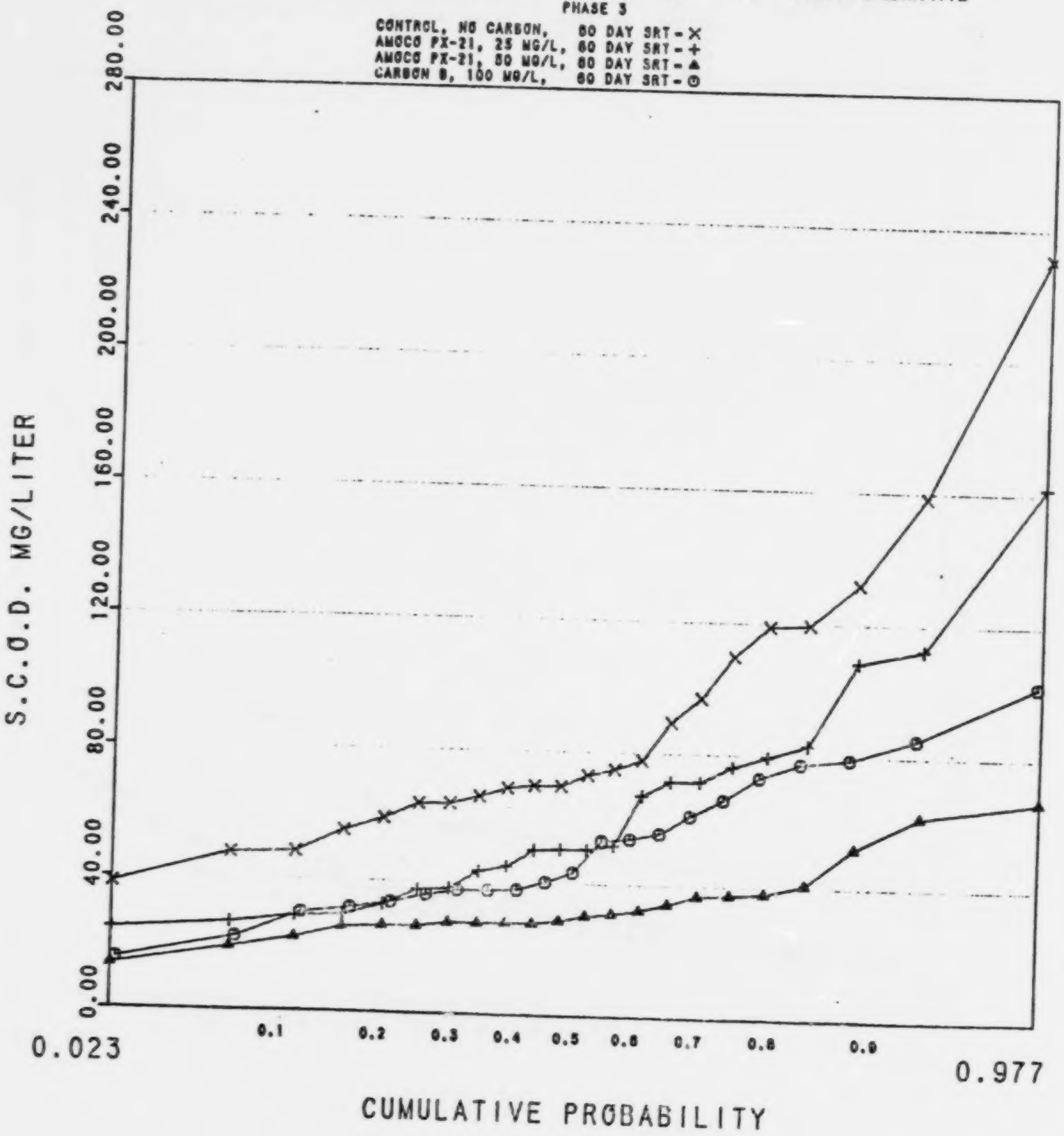


FIGURE 6 - AMMONIA-NITROGEN - PHASE 3

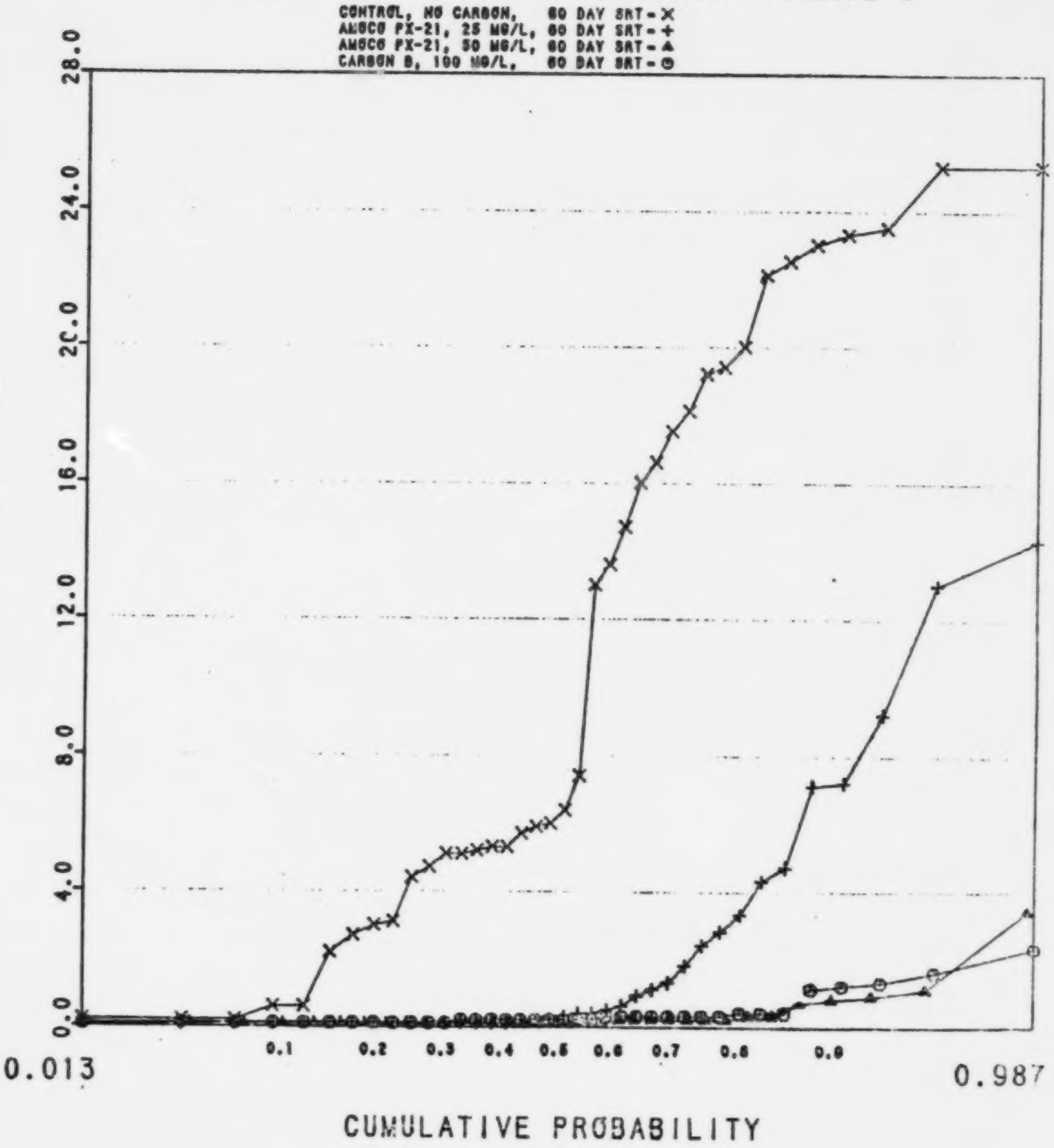
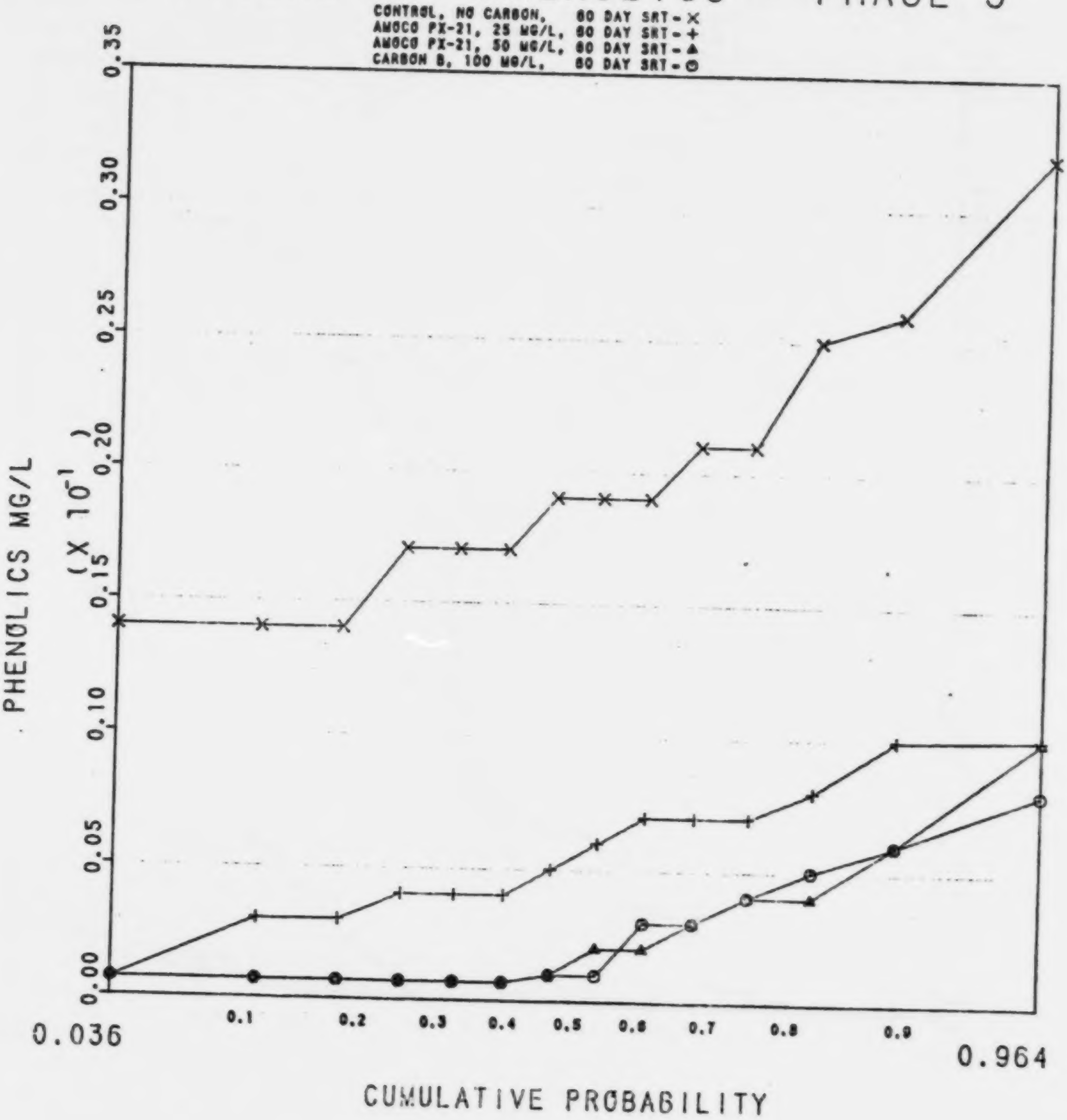


FIGURE 7 - PHENOLICS - PHASE 3



"TREATMENT OF OIL REFINERY WASTEWATERS WITH POWDERED ACTIVATED CARBON"

Paschal B. DeJohn
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James P. Black
Industry Coordinator, ICI United States Inc. (Delaware)

INTRODUCTION

The effectiveness of powdered carbon as an additive to improve activated sludge treatment has been demonstrated in a variety of industrial and municipal plants. This type of treatment has gained wide acceptance in the past few years and is currently an essential part of treatment at 60-80 plants. These plants range in size from 10,000 gpd package units located along the Alaska Pipeline to the very sophisticated 40,000,000 gpd PACT treatment plant at the DuPont Chambers Works in Deepwater, New Jersey. At least four petroleum refiners currently use powdered carbon as an integral part of their waste treatment scheme.

HOW THE PROCESS WORKS

The reason powdered carbon has gained such acceptance treating a wide variety of waste streams is the extreme flexibility which can be employed in its usage.

- The amount of carbon used can be varied to meet the treatment requirements as they change.
- Higher COD or BOD removal than is usually obtainable by conventional biological treatment can be achieved.
- The combination of activated carbon in a biological system provides more effective treatment than either of the processes would if used singularly.

Carbon aids the biological process two ways:

1. By direct adsorption of pollutants.
2. By providing a more favorable environment for the microorganisms to propogate.

Adsorption is an equilibrium phenomenon. In general, carbon preferentially absorbs higher molecular weight compounds. Given a related series of organic compounds; for example, alcohols, one finds that the lower molecular weight alcohols (methanol, ethanol) are not appreciably absorbed by carbon while the higher molecular weight alcohols are. Fortunately, compounds which are poorly absorbed (weakly held by the carbon) are usually compounds which are the most amenable to biological treatment.

We can generally classify organic compounds into three broad categories with respect to their adsorptability onto carbon.

1. Compounds which are readily adsorbed. These compounds are usually "tightly held" by the carbon. And consequently, they are not readily desorbed.
2. Compounds which are adsorbed with difficulty. These compounds are desorbed easily.
3. Compounds which are poorly adsorbed.

Organic compounds can also be classified in terms of their susceptibility to biodegradation:

1. Compounds which are readily and rapidly biodegraded.
2. Compounds that are degraded slowly.
3. Compounds that are not biodegraded. Many of these can function as toxicants in a biological system.

It is important for one to understand the interaction of carbon and the microorganisms present in an activated sludge system. Exhibit 1 does this by considering how a carbon-biological system handles each of the above classifications of organics compounds. Relative adsorptivity and biodegradability for organic compounds was taken from an EPA source (Reference 1).

The boxes in Exhibit 1 have been numbered from 1 through 9 and are interpreted as follows:

Box	Degree of Biodegradability	Adsorptability
1	Rapid	Strong
2	Rapid	Moderate
3	Rapid	Weak
4	Slow	Strong
5	Slow	Moderate
6	Slow	Weak
7	None	Strong
8	None	Moderate
9	None	Weak

The classes of compounds which are represented by boxes 1, 2, and 3 would be handled quite easily by the microorganisms in a carbon-biological system. Those compounds which are represented by boxes 1, 4, and 7 would be removed by direct adsorption on the carbon. Compounds which fall in box 1 (both rapidly biodegradable and strongly adsorbed) are few in number. The only example that we could find is o-cresol.

Boxes 4, 5, and 6 represent compounds which are slowly biodegradable. These compounds probably would not be removed very effectively in a conventional activated sludge system. In a carbon-biological system, compounds in box 4 are removed by direct adsorption and are held very tightly by the carbon. Compounds in boxes 5 and 6 are retained in the system by moderate or weak adsorption. Because carbon is adsorbing these compounds, their concentration in the liquid stream is reduced. The microorganisms are able to degrade the organics in reduced concentrations, and as they do the equillibrium between the carbon and these organics in the waste is disturbed. Because these compounds are not held very tightly by the carbon, they are readily desorbed back into the system and a new equillibrium is established. In this fashion, the carbon is acting as a storage area keeping the concentration of slowly biodegradable organics at a level where they can be handled by the microorganisms. Compounds which fall into the categories represented by boxes 4, 5, and 6 are effectively handled in a carbon-biological system because of synergistic effects. It is primarily these compounds that are removed more effectively in a carbon-biological system as compared to either process operating singularly.

Compounds represented by boxes 7, 8, and 9 are not biodegradable. And in some cases, these compounds are actually toxic to microorganisms. In our opinion, carbon performs its most beneficial action in this area. Compounds which fall into the category represented by box 7 are removed by direct adsorption and are held very tightly by the carbon. Compounds in box 8 are removed by direct adsorption, and even though they are held very loosely by the carbon, it is difficult to disturb the equillibrium. This is because the concentration of these organics remaining in the waste stream are not being degraded by the microorganisms. The compounds represented by box 9 are the only ones that cannot be handled very effectively in a carbon-biological system. Fortunately, there are very few organics which are both nonbiodegradable and weakly adsorbed by carbon.

Examples of the different compounds are shown in the various boxes in Exhibit 1.

One of the important effects of carbon in the system (not related directly to adsorption) is the higher levels of biomass that can be used because of the density and "weighting effect" of the carbon. (Both the use of greater sludge mass and the temporary retention of slowly degraded compounds by the carbon gives more time for the compounds to be consumed biologically).

Carbon adsorbs the pollutants and oxygen, localizing them for bacterial attack. Because the aerobic action is dependent upon the concentration of the reactants, this localizing effect serves to drive the reaction further towards completion resulting in improved BOD removal (Reference 2).

Many pollutants that are not biologically degraded in a conventional activated sludge system would be if they were in contact with the biomass for a longer period of time. When absorbed by the carbon, these molecules settle into the sludge. Contact time is thereby, extended from hours to days. This results in lower effluent COD's and TOC's. High density powdered carbons improve solids settling in the secondary clarifiers. This results in lower effluent suspended solids and also a reduction in BOD. Under high organic load conditions which normally would lead to sludge bulking, the dense carbon will act as a weighting agent keeping the sludge in the system. When dispersed biofloc results due to low organic loads, carbon serves as a seed for floc formation preventing loss of solids. Under these conditions, phosphorous and nitrogen removal are generally enhanced.

Powdered carbon improves treatment in activated sludge process because of its adsorptive and physical properties. Powdered carbon can be added to any convenient point in the activated sludge process to get it into the aerator. Direct addition to the aerator, sludge return lines, influent channels, or through the secondary clarifier are all possibilities. It is not necessary to add carbon continuously in most cases. A dense, easily wetted carbon can be added dry or in slurry form with water.

RESULTS

14 refineries have evaluated HYDRODARCO powdered activated carbons in full scale activated sludge systems during the past three years. The first treats a 2.2 MGD flow with an average BOD of 400 ppm in a 1.2 million gallon aerator. Mixed liquor solids are maintained at 3600 ppm (2880 ppm volatile). Waste activated sludge is digested aerobically, centrifuged, and hauled to landfill. Despite a secondary clarifier overflow rate of only 423 gallons/ft.^{2} and use of 22 ppm cationic polymer for secondary solids capture, effluent solids averaged in excess of 100 ppm. Toxic loads caused periodic loss of aerator biosolids. Defoamer costs averaged $200/day for aerator foam control.

HYDRODARCO C, a high density, lignite based powdered carbon, was added to the aerator over a four and one-half month period. Eventually, the equilibrium carbon level reached 1800-2000 ppm. At the sludge solids concentration obtained and wasting rates employed, it was possible to maintain this level with a daily average carbon dose of only 20 ppm.

Over the entire carbon test period, average BOD reduction equaled 82% versus 23% during the post test control period (Figure 1). As carbon built up in the system, BOD removals reached the 90-95% range, and the plant was able to meet their 30 ppm BOD effluent standard. Effluent COD was reduced from an average of 1180 ppm without carbon to 350 ppm with (Figure 2). Average effluent TOC decreased from 420 ppm to 100 ppm (Figure 3), and total carbon decreased from 520 ppm to 180 ppm (Figure 4). The lower slope of the carbon plots also indicate the decreased variability in effluent quality with carbon present.

HYDRODARCO C had a dramatic effect on the reduction of oil through the system (Figure 5). The effluent concentration was reduced by 75% (average), and the range was narrowed as well.

Both removal of the oil by the powdered carbon and the weighting effect of carbon resulted in lower effluent solids (Figure 6). Prior to carbon treatment, the plant used polymer at a dosage of 20 ppm, but still experienced poor solids settling. When carbon was added to the system, solids settling improved, and the polymer dosage was cut in half. Since effective solids settling could not be achieved with the use of carbon or polymer alone, it appears that the combination of the two was required to attain the desired results. This, of course, represents an operating cost savings for the plant.

Improved solids settling increased sludge thickening which allowed a 65% reduction in sludge wasting. Again, savings on the operation of the centrifuges, including power and labor, occurred.

Use of HYDRODARCO C eliminated the need for aerator defoamer. Removing the foaming agents from the wastewater by adsorbing them eliminated foam problems in the receiving stream. Defoamers only suppress foam in the aerator and do not prevent its reappearance in the effluent. Carbon can reduce operating costs by allowing surface aerators to aerate and mix the activated sludge rather than expand energy generating foam.

Both nitrogen (Figure 7) and phosphorous (Figure 8) removals were improved with powdered carbon. Reason: carbon adsorbs compounds toxic to nitrifiers and allows them to operate at normal levels. In this waste, neither nitrogen nor phosphorous were limiting for bacteria growth. Increased nitrogen removals are attributed to the fact that the dense carbon settled the nitrifying organisms which normally would float out of the system. The result is a longer solids retention time which is more favorable for nitrification to occur. By the same token, improved solids settling is probably the reason for decreased phosphorous levels. We suspect that the phosphorous is precipitated with the carbon-biosolids floc and removed in the sludge rather than degraded biologically.

While the exact reason for the bug kills prior to carbon was not known, upsets were greatly reduced with carbon in the aerator. A possible explanation is the effect carbon had on the removals of heavy metals such as zinc (Figure 9). The ability of activated carbon to adsorb heavy metals from wastewater has been established elsewhere (References 3, 4, and 5).

The second evaluation was conducted at a 12 MGD plant treating an average 12 MGD flow. The TOC of the raw waste ranged from 100-1000 ppm, averaging about 200 ppm. Major treatment problems included aerator foaming caused by alkanolamines in the waste; high effluent TOC; oily, difficult-to-handle sludge; and high effluent solids.

Effluent TOC's were maintained below 20 ppm during shock load periods. This was well within the standard of 50 ppm. In a post test control phase, a deterioration in effluent quality was observed as carbon was lost from the system through sludge wasting.

A third evaluation was conducted at a 2.5 MGD plant treating a 550 ppm COD refinery waste in a two stage, conventional activated sludge system. Carbon was added to the second stage aerator over a six week period. A constant daily carbon dose was maintained for each week and increased in succeeding weeks. No sludge was wasted intentionally during this time.

Optimum treatment was found at relatively high influent dose of 200 ppm. Effluent solids and COD removals increased 40%, and BOD removals, already high, increased 10%.

The major finding of this study was the increased removals of cyanide with carbon in the aerator. In conjunction with $CuSO_4$ treatment, the average cyanide levels decreased from 1 ppm before carbon to 0.05 ppm. The precise nature of this removal is not known and bears further investigation.

Results from a fourth study are summarized in Exhibit R for three separate carbon addition periods. This plant is a current user of activated carbon to treat 2.2 MGD flow. They have reported the following results from carbon addition (Reference 6):

56% reduction of suspended solids.
36% reduction of COD.
76% reduction of BOD.
Foam problem elimination.

This improved plant performance is achieved at a carbon cost of 1.7-4.3¢/1000 gallons treated.

A fifth study was made at a refinery which had a 6 MGD (8 MGD design) activated sludge plant. Carbon dosage reached approximately 500 ppm in the aerator before the study was terminated due to loss of biosolids. The loss of biomass resulted from an inadvertent increase in sludge wasting. This plant continued to use the same volumetric wasting rate when carbon was added to the system and because of the sludge density increase due to carbon addition, the MLVSS dropped sharply from 2900 ppm before carbon to 1500 ppm at the conclusion of the study. After carbon addition was stopped, the MLVSS returned to 2500 ppm with no change in the wasting rate.

Although considerable improvement in BOD removal was achieved at this plant (Exhibit S), the full benefit of carbon was not realized because of high influent oil concentrations (100+ ppm).

SUMMARY & CONCLUSIONS

- In summary, it has been shown that refinery wastes can be successfully treated with powdered carbon in activated sludge.

- Powdered carbon can improve organic removals, aid solids settling and sludge handling, and provide protection from toxic or shock loadings. In the face of widely varying influent organic or hydraulic loads, carbon levels effluent quality.

- High density carbons are preferred to minimize carryover from secondary clarifiers and to increase sludge compaction. Such carbons also require less makeup to maintain the desired aerator equillibrium level since carbon is lost from the system only during sludge wasting.

- Normally, one would think that the use of carbon would increase costs. However, savings on defoamers, coagulants, powder and labor can often decrease operating expenses.

BIOGRAPHY

Mr. Paschal DeJohn is Manager of Purification Sales and Project Leader in Activated Carbon at ICI United States Inc.; holding this position since 1972. Mr. DeJohn holds a B.S. degree in chemistry from Westchester State College and an M.B.A. degree from Widener College, Pennsylvania. Previous to his present position Mr. DeJohn was Water & Wastewater Treatment District Engineer with Drew Chemical, Parsippany, New Jersey. He is 1977 Technical Conference Chairman for WWEMI and the 1978 General Conference Chairman for this ame organization. Mr. DeJohn has been involved with water and wastewater treatment for the past twelve years.

James P. Black is Industry Coordinator for Water Purification at ICI United States Inc. He has a B.S. degree in chemical engineering from the University of Texas at Austin. Prior employment included ICI's Research & Development Laboratory, and Corporate Planning Staff.

DEJOHN PAPER DISCUSSION

Ed Sebesta, Brown & Root: Have you observed any situations where you mentioned some compounds are loosely adsorbed or difficultly adsorbed and then quite easy to be desorbed? Have you ever seen any situations or heard of situations where because of changing influent situations you may suddenly desorb an accumulation of adsorbed materials and effect the system in that way?

DeJohn: Potentially that can occur. I would think something like that would be more prone to happen in a granular carbon system. You can design a granular carbon system around this however. In the PACT systems we've been involved in, I'm not aware of any that have desorbed back an accumulation of adsorbed material. But there's always the possibility that this can happen.

REFERENCES

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3. Esmond, S. E. and Petrasek, A. C., "Removal of Heavy Metals by Wastewater Treatment Plants," presented at the WWEMA Industrial Water and Pollution Conference, Chicago, Illinois, March 14-16, 1973.

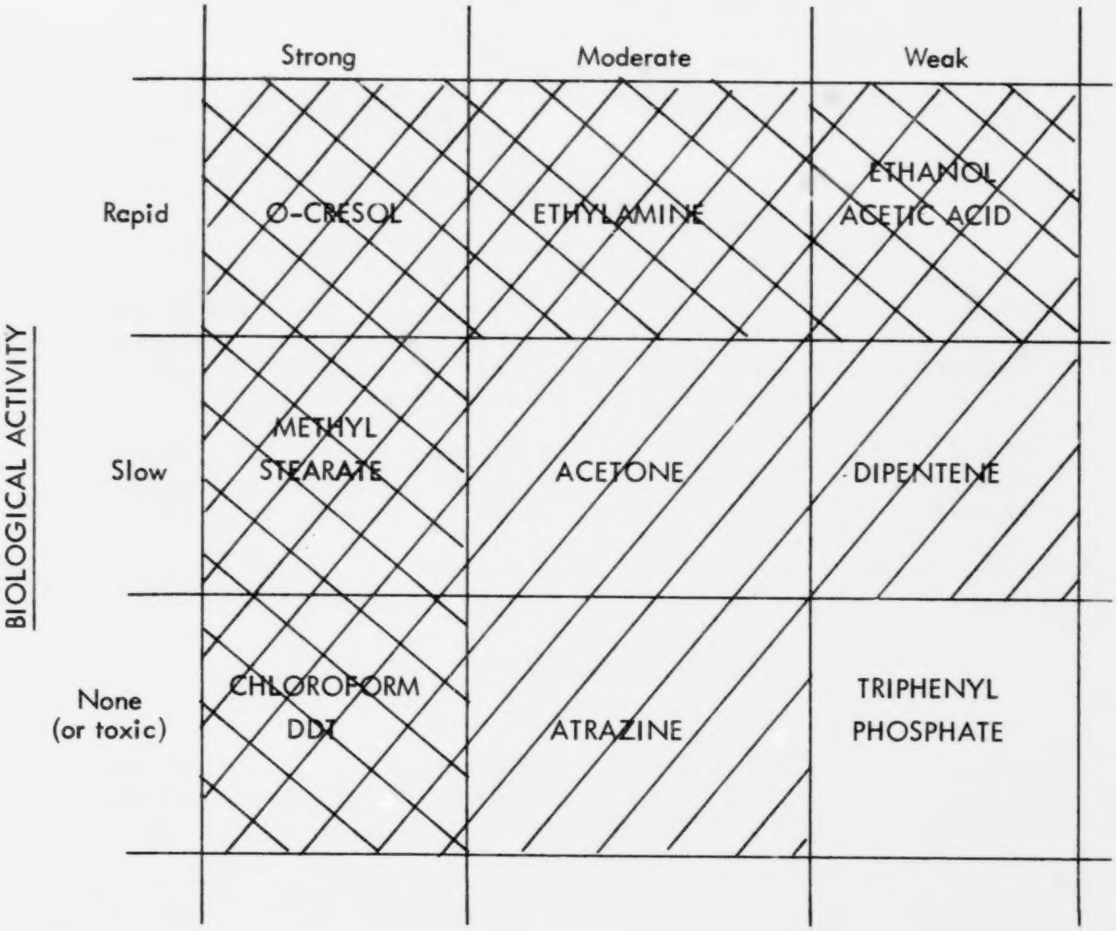
4. Sigworth, E. A. and Smith, S. B., "Adsorption of Inorganic Compounds by Activated Carbon," Journal AWWA, Water Technology/Quality, June, 1972 (p. 306).

5. Linstedt, K. D. et. al, "Trace Element Removals in Advanced Wastewater Treatment Processes," Journal WPCF, 43, No. 7, 1507 (July, 1971).

6. Rizzo, Joyce A., "Case History: Use of Powdered Activated Carbon in an Activated Sludge System", presented at the Open Forum on Management of Petroleum Refinery Wastewaters, Tulsa, Oklahoma, 1976.

EXHIBIT 1

CARBON ADSORPTION



BIOLOGICAL ACTIVITY	Strong	Moderate	Weak
Rapid	O-CRESOL	ETHYLAMINE	ETHANOL ACETIC ACID
Slow	METHYL STEARATE	ACETONE	DIPENTENE
None (or toxic)	CHLOROFORM DDT	ATRAZINE	TRIPHENYL PHOSPHATE

EXHIBIT R

	No Carbon	First Carbon Period
COD		
Influent	459 ppm	457 ppm
Effluent	170 ppm	135 ppm
% Removed	63	70
BOD		
Influent	152 ppm	213 ppm
Effluent	15 ppm	15 ppm
% Removed	90	93
SUSPENDED SOLIDS		
Effluent	115	50
COD		
Influent	343 ppm	444 ppm
Effluent	266 ppm	183 ppm
% Removed	23	59
BOD		
Influent	152 ppm	227 ppm
Effluent	30 ppm	14 ppm
% Removed	80	94
SUSPENDED SOLIDS		
Effluent	162	72
COD		
Influent	367 ppm	379 ppm
Effluent	166 ppm	112 ppm
% Removed	55	70
BOD		
Influent	188 ppm	207 ppm
Effluent	12 ppm	3 ppm
% Removed	94	99
SUSPENDED SOLIDS		
Effluent	79	42

EXHIBIT S

Flow: 8 MGD design, 6 MGD actual.

Carbon Dose: 500 ppm in aerator.

MLVSS: 2900 ppm before carbon
1500 ppm during carbon

(A 50% loss of aerator solids resulting from continuing same volumetric wasting rate of the more dense carbon sludge.)

2500 ppm after carbon

- BOD removal - 55% before carbon addition
  70-80% during carbon addition
  60% after carbon addition
- Influent oil concentrations were so high (100+ ppm) during test that effects of carbon were overshadowed.

EFFECT OF POWDERED CARBON ON
BOD REMOVAL

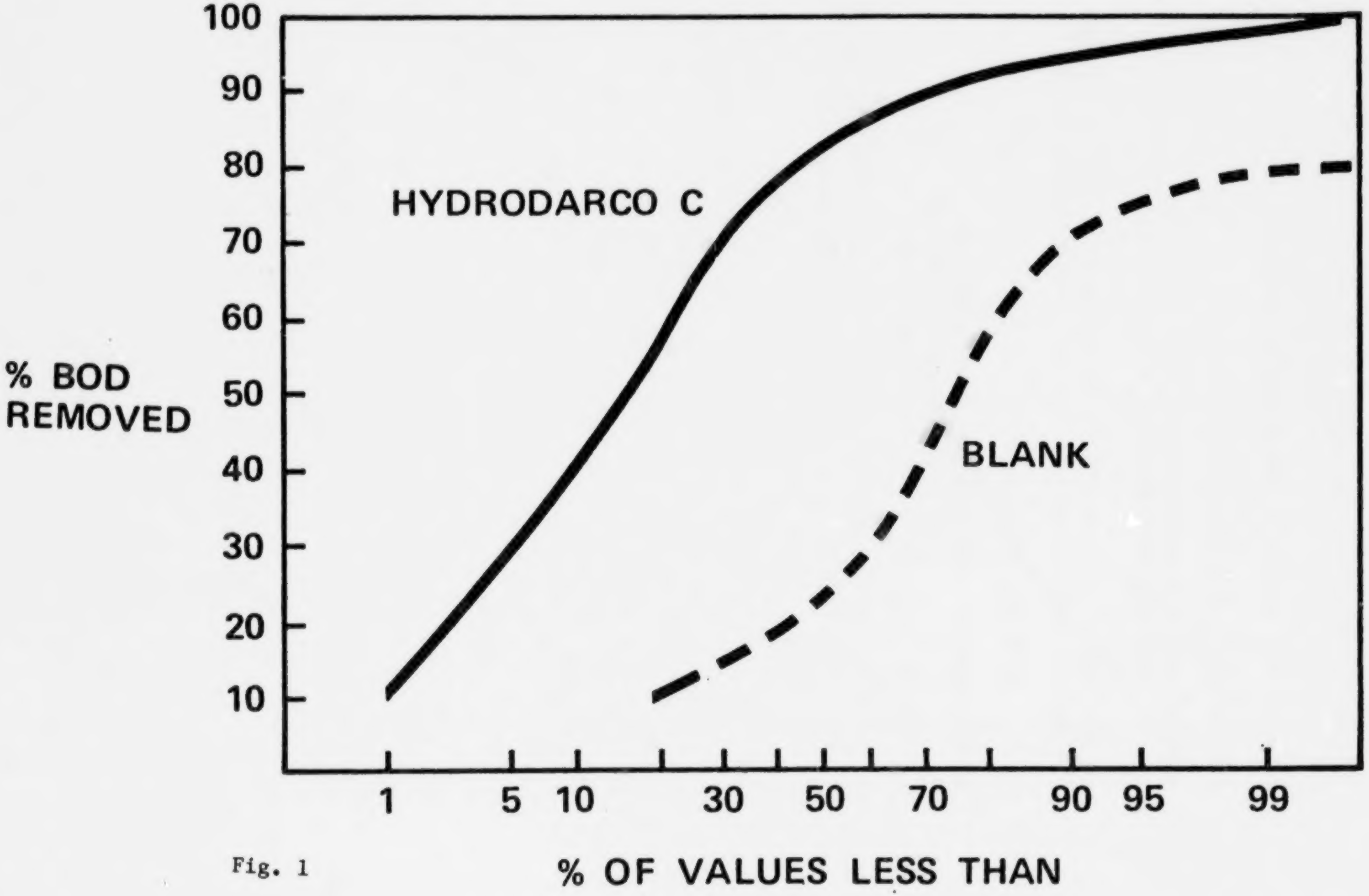


Fig. 1

EFFECT OF POWDERED CARBON ON EFFLUENT COD

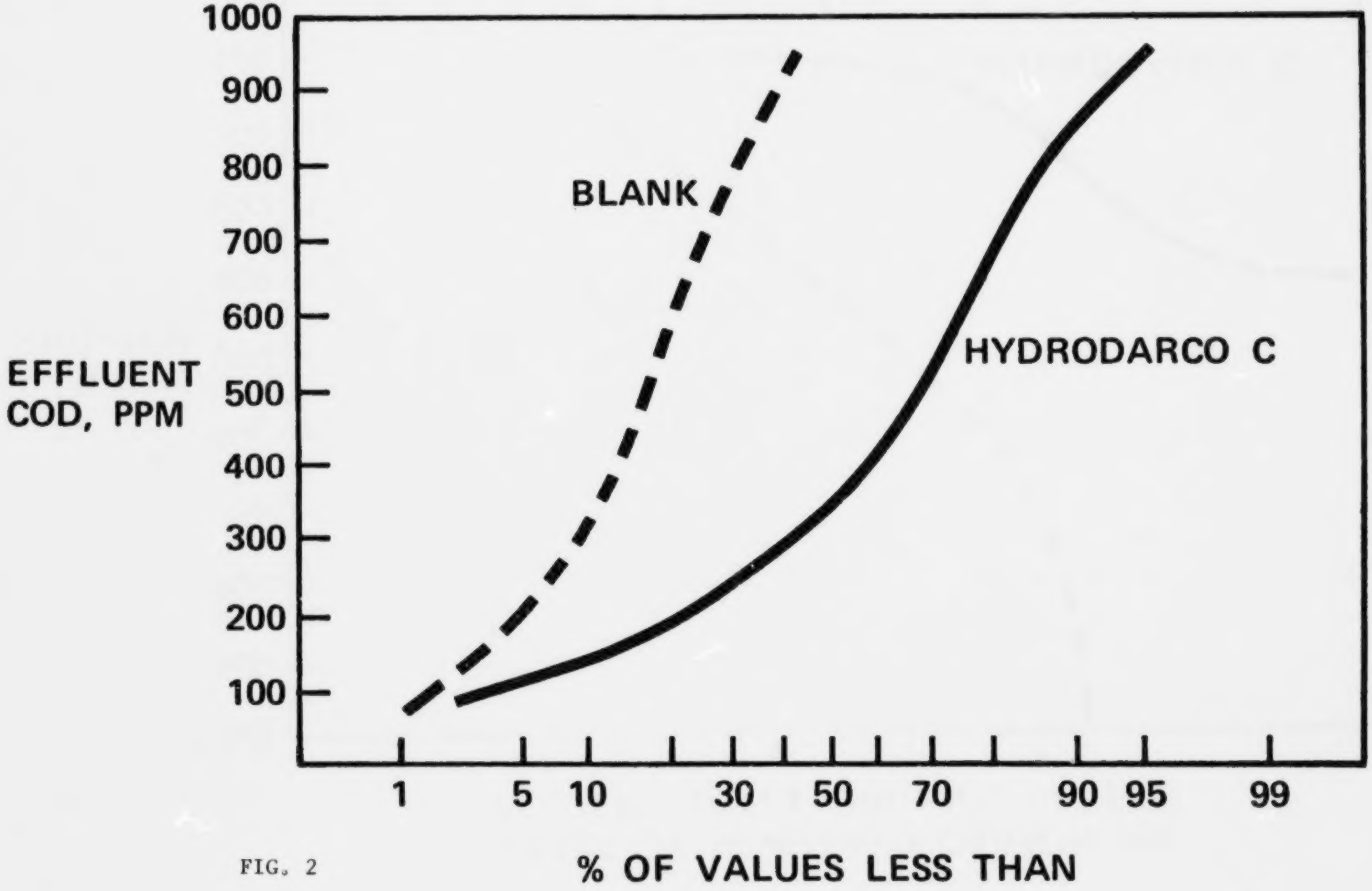
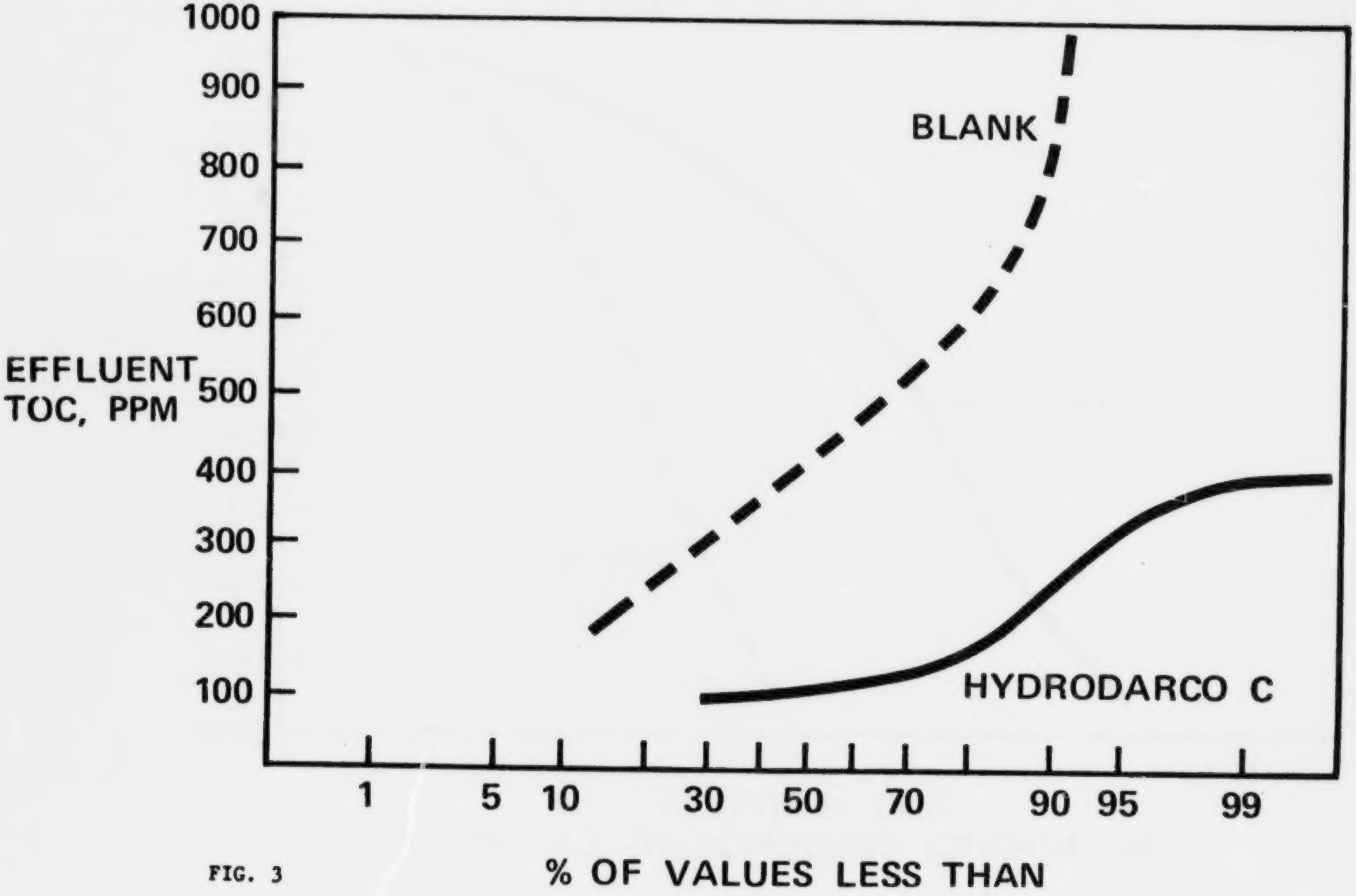


FIG. 2



EFFECT OF POWDERED CARBON ON EFFLUENT TOTAL ORGANIC CARBON

FIG. 3

EFFECT OF POWDERED CARBON ON EFFLUENT TOTAL CARBON

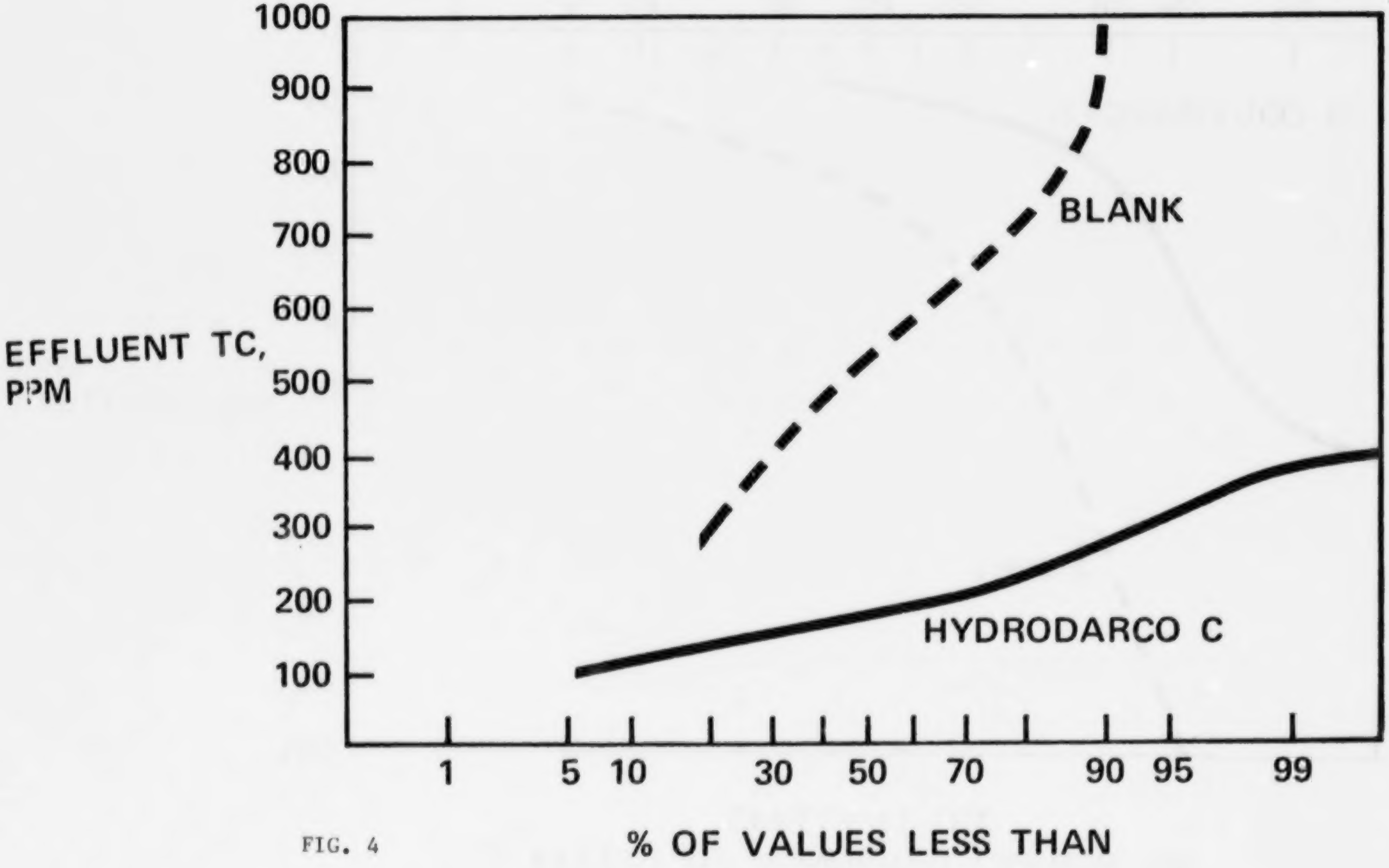


FIG. 4

EFFECT OF POWDERED CARBON ON EFFLUENT OIL

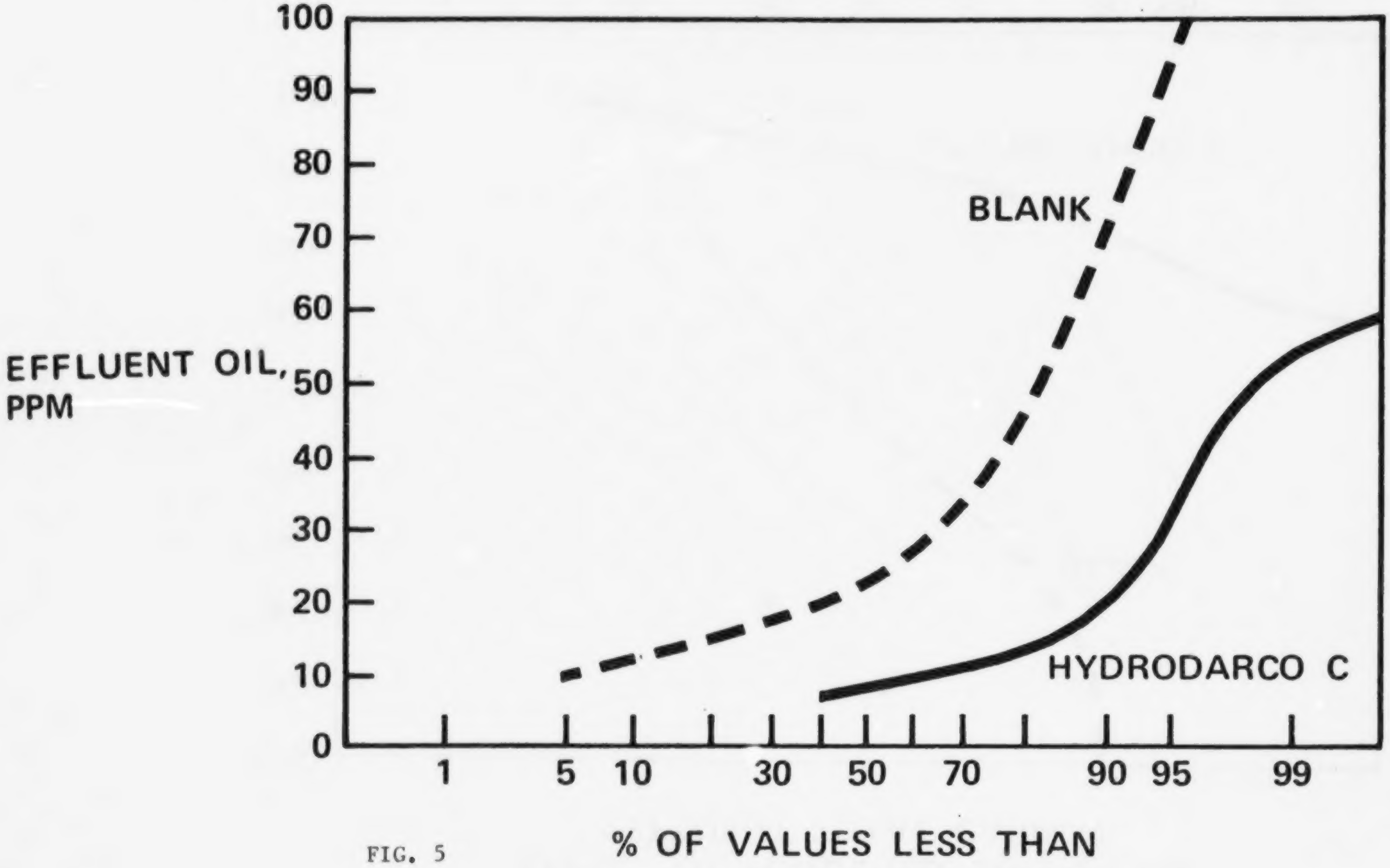


FIG. 5

EFFECT OF POWDERED CARBON ON EFFLUENT SUSPENDED SOLIDS

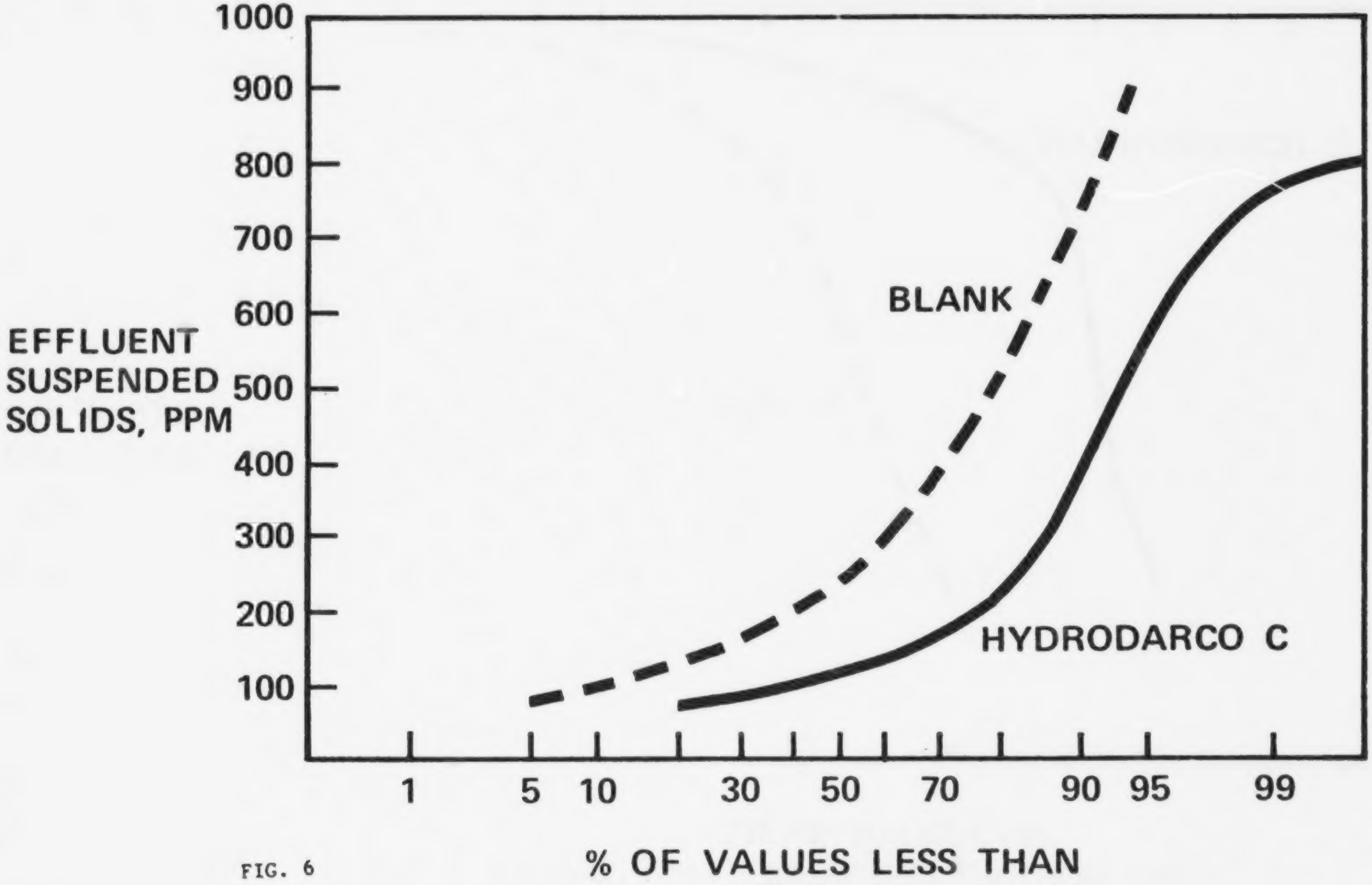


FIG. 6

EFFECT OF POWDERED CARBON ON EFFLUENT NITROGEN

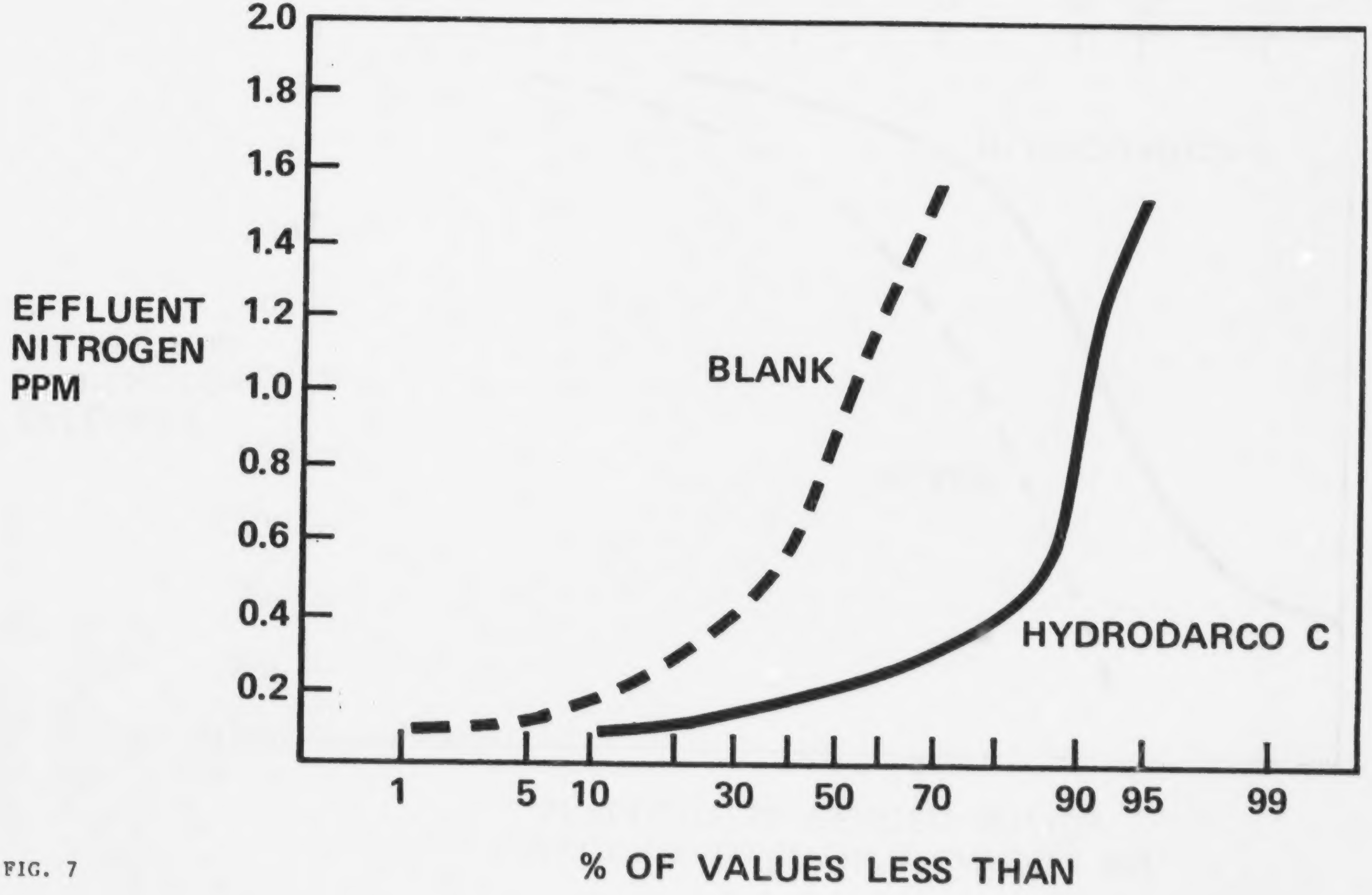


FIG. 7

EFFECT OF POWDERED CARBON ON EFFLUENT PHOSPHOROUS

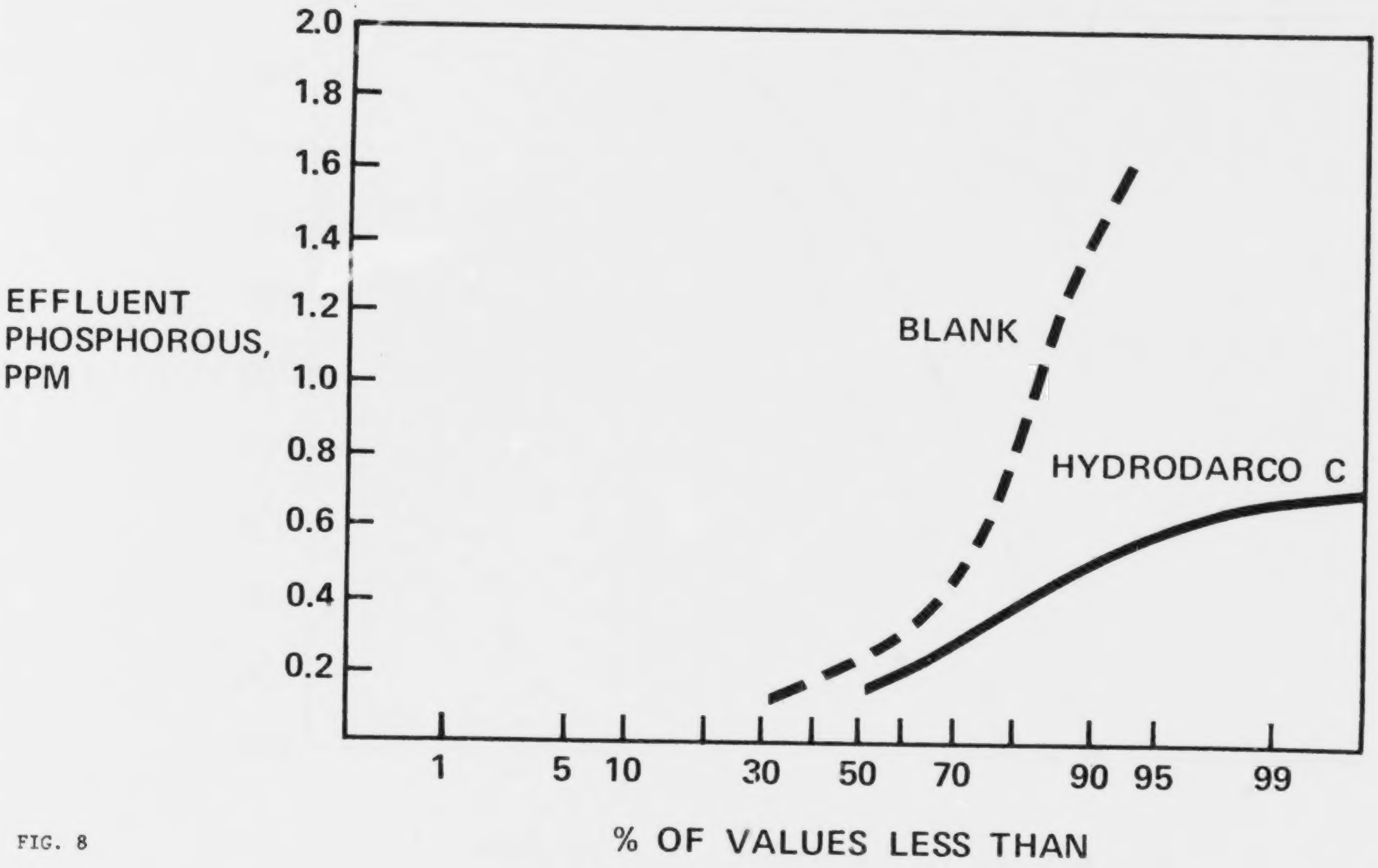


FIG. 8

EFFECT OF POWDERED CARBON ON
EFFLUENT ZINC

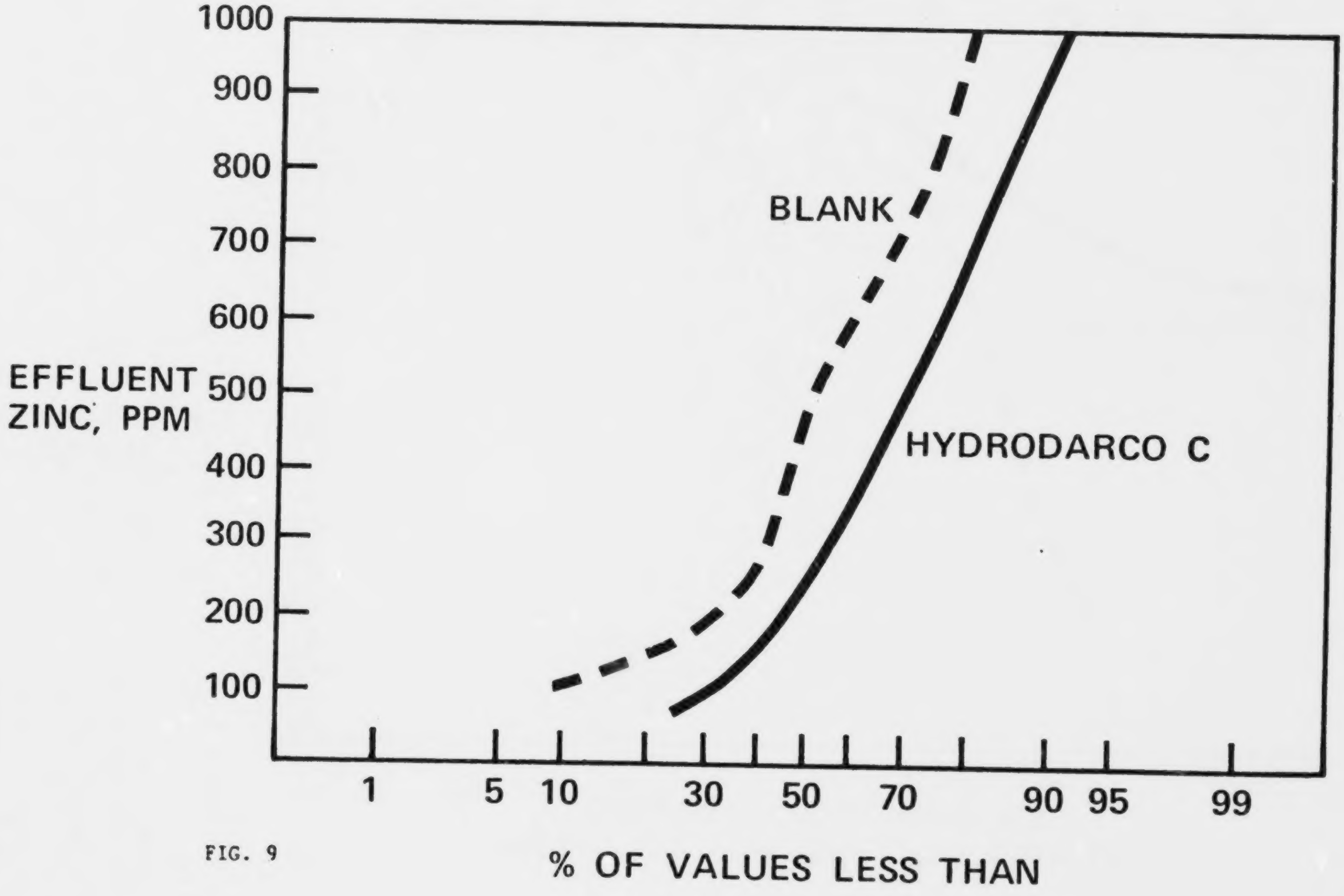


FIG. 9

SECTION 5

Full-Scale Granular Activated Carbon Treatment

ACTIVATED CARBON TREATMENT OF COMBINED STORM AND PROCESS WATERS

M. A. Prosche
Atlantic Richfield Company, Watson Refinery, Carson, California

The Watson Refinery of the Atlantic Richfield Oil Company is located adjacent to the Dominguez Channel in Los Angeles County. This Channel is a non-navigable dredged tidal estuary which is lined with rip-rap and used specifically for the discharge of refinery and chemical plant waste waters and for rain water runoff.

In 1968, the Los Angeles Regional Water Quality Control Board made a study of the Dominguez Channel and determined that petroleum and chemical plant discharges were causing a problem due to the oxygen demand of their waste waters entering the Channel. The Control Board, in accordance with these findings, issued a resolution in February, 1968, which limited the total chemical oxygen demand (COD) from all industrial discharges into the Channel. These discharges also included any contaminated rain water runoff. The resolution was to be complied with by February, 1971.

As defined by the resolution, the Watson Refinery was limited to 1330 pounds per day of COD in its discharge water to the Channel. Meeting this requirement meant reducing the COD in its discharge waters by 95 per cent.

Fortunately, the Watson Refinery as a taxpayer of Los Angeles County was able to make arrangements with the Los Angeles County Sewer District to have its process waste water handled in the County's primary treatment unit. However, due to limitations in the County unit, the County was unable to handle rain water runoff. This presented a problem for the Watson Refinery due to the fact that the rain water collection facilities were interconnected with the process waste water collection system. Therefore, during periods of rainfall, the process waste water and rain water mixture could not be sent to the sewer district facilities, nor could it be sent to the Dominguez Channel due to high COD content of the process waste water.

To solve this problem a system was needed which would treat all the process water plus rain water during the rainy season for the removal of COD and allow its discharge to the Channel. A system was needed which could be started up easily when rain fell and then shut down when no longer required. The system selected was impounding of rain plus process water during the storm followed by activated carbon treatment to adsorb the COD material.

ADSORPTION SECTION DESIGN AND DESCRIPTION

Since it was planned to operate the plant only during the rainy season, it was felt there was no need to design for continuous carbon regeneration and changeout of the beds. Therefore, the design was based on use of only the carbon beds during the rainy season, and then regeneration of all the beds during the dry summer months in preparation for the next rainy season. The significant design criteria for the plant and impounding basin were as follows:

Design Criteria

Flow Rate	100,000 BPD 3,000 GPM
Inlet COD	250 ppm
Outlet COD	37 ppm
Impounding Basin	1.2 million barrels capacity

Following the accumulation of 0.1 inches of rainfall, regulations call for diverting process water from the sewer system. This is accomplished automatically by means of a solenoid operated valve actuated by a rain gauge. Process water plus commingled rain water is then switched to the 1.2 million barrel impounding basin. Depending upon the specific situation, the carbon plant can be started up immediately for discharge to the Channel or it can be started up later following the rain. A flow diagram of the adsorption section of the plant is shown in Figure 1.

Impounded water is delivered to the plant through a 14" line from the basin. The water is then delivered to a distribution trough where it is distributed to 12 adsorber cells by adjustable slide gates. Each of the twelve cells is 12' by 12' square and 26' feet deep. Each cell originally contained 13' of carbon having a dry weight of about 50,000 pounds.

The water passes down through the carbon bed where it collects in the underdrain system. Supporting the carbon is a one-foot layer of gravel on top of a Leopold tile underdrain system. The treated water then flows through 6" lines from each cell to a 24" collection header leading to the effluent retention sump. Each 6" discharge line has a sample point and an air-operated pinch valve which can be shut during backwashing.

If necessary to further control COD, a chlorine-water solution may be injected into the incoming treated water stream. Approximately 15 minutes retention time is allowed for chlorine contact in this sump. From the sump the water flows by gravity to the Channel.

Each carbon bed must be backwashed whenever it will not pass its share of water flow due to buildup of solids on top of the carbon. This is indicated by the rise in the level of the water in each carbon cell. When the level rises to the height of the backwash troughs, the flow to and from the bed is stopped, and treated water from the backwash sump is pumped up through the bed to expand it and flush out accumulated solids. The turbid water overflows into the backwash troughs to the backwash effluent sump where it is pumped back to the reservoir for settling and retreating.

EPA DEMONSTRATION GRANT

Following completion of the plant, a demonstration grant was received sponsored by the Water Quality Research Division of Applied Science and Technology of the Environmental Protection Agency. The specific objectives of the demonstration project were as follows:

1. Determine feasibility of activated carbon as a treatment system for storm runoff and refinery process waters.
2. Evaluate performance of the system.
3. Determine operating costs.
4. Assess reliability of the system.

The report relative to this project has now been published by the EPA.

ADSORPTION SECTION OPERATION AND PERFORMANCE

The carbon plant was first placed in operation in May, 1971 for some preliminary test work prior to the rainy season. At that time the test water was synthesized using process water diluted with service water. Operation with rain water and process water was not required until later that year in December. At that time sufficient rain fell to require placing the unit in full operation at the design rate of 3,000 gpm total to all twelve cells. Subsequent to that a total of 6 runs were made processing impounded water from the intermittent rain storms that followed. The performance data for all of these runs are shown in Table 1.

Typical Performance Data First Rainy Season

Table 1

Run Number	Length of Run, Hours	Feed Rate, GPM	Average COD Feed	Average COD Effluent
1	44	3000	326	43
2	48	3000-2000	360	48
3	38	2000	374	86
4	18	2000	310	67
5	95	1000	237	100
6	22	2000	147	93

During the initial runs the COD of the feed was higher than design and the plant was unable to produce the desired removal. Therefore, the feed rate was reduced to 2,000 gpm. Even at this lower rate the effluent COD content was greater than the regulations allowed and feed rate was again reduced to 1,000 gpm. By the end of the season the reservoir COD had dropped to 147 ppm due to rain dilution and the rate was increased to 2000 GPM. However, performance continued poor even at this low concentration.

A good evaluation of the performance of the plant during this first season of operation is difficult due to the significant variations in feed COD and the necessity of having to reduce the feed rate from 3000 to 1000 gpm. However, COD data for each cell was recorded during the course of the run and some generalizations are possible. At the end of the season the COD loading in each cell varied from 0.2 pounds of COD per pound of carbon to a high of 0.3 pounds of COD per pound of carbon. During the season a total of 52,000,000 gallons of water were processed. The average feed COD concentration was 377 ppm while the effluent averaged 67 ppm. The carbon loading averaged 0.23 pounds COD per pound of carbon. It also appeared that the potential maximum carbon loading at a constant effluent COD concentration was quite sensitive to the COD of the feed.

Other data collected during the first season's operation included measurement of the carbon's adsorptive ability at various depths in the bed after a period of operation. One of the cells was taken out of service after 208 hours of operation and the carbon was sampled at various depths to test its relative adsorptive efficiency as compared to virgin carbon. The data are shown in Figure 2. The data show that the top two feet of carbon were completely exhausted while the last five feet were still 65 per cent of virgin adsorptive ability.

Prior to the second rainy season, we made several significant changes in operation. In order to increase the adsorptive capacity of the unit, 15,000 pounds of carbon were added to the existing 50,000 pounds in each of the cells. This increased the bed depth from 13 feet to 17 feet. It was also decided to recycle effluent water back to the feed in order to control the feed COD to a concentration of not greater than about 250 ppm. This change in operation was made after noting during the first rainy season of operation that the effluent COD level varied directly with the feed COD concentration and the specification COD quantity to the channel would be exceeded during periods of high feed COD. It was also felt that controlled feed COD would allow a higher ultimate COD loading of the carbon. One other modification made was the aeration of the effluent recycled back to the feed to prevent growth of anaerobic bacteria in the beds.

For the second rainy season of operation, we elected to operate part of the plant on a continuous basis, regenerating each bed as it became spent, and returning the regenerated carbon for use again. To accomplish this five of the cells were placed in continuous staggered operation along with the regeneration furnace. This was the largest number of cells operating in a progression mode that could be accommodated by the capacity of the regeneration furnace. The remaining seven cells were used for once-through processing as was done during the first rainy season. In all cases the flow to each cell was held constant at 250 gpm which included the waste water feed from the reservoir plus the recycle dilution.

Typical performance data for one of the five cells operated in staggered mode are shown in Figure 3. This figure shows the relationship between feed and effluent COD and the COD loading on the carbon. During initial operation of this cell, it was elected to discontinue service and regenerate after the effluent from the cell reached a COD concentration of about 50 ppm. This corresponded to a carbon loading of 0.20 pounds of COD per pound of carbon and a run length of 22 days.

The carbon was regenerated and returned to the same cell. In the second run the cell was allowed to operate until the effluent reached a COD concentration of about 100 ppm. This corresponded to a carbon loading of 0.40 pounds COD per pound of carbon and a run length of 38 days.

The performance of the seven cells that were operated on a once through basis with no regeneration is shown in Figure 4. Effluent COD concentration was allowed to reach 50 ppm before all the cells were shut down for later regeneration. As shown in the figure, the corresponding carbon loading attained in all of these cells was 0.30 pounds COD per pound of carbon and the run length was approximately 30 days.

The evaluation of performance of the carbon plant for this second rainy season was again based on the combined operation of all the cells. During the season a total of 102,000,000 gallons of water were processed. The average diluted feed COD concentration was 233 ppm while the effluent averaged 48 ppm. The carbon loading averaged 0.26 pounds COD per pound of carbon.

A summary of the performance of the plant during the two rainy seasons of operation is shown in Table 2.

Adsorption Data
Table 2

Commercial Operation	Feed COD, PPM Average	Effluent COD, PPM Average	Carbon Loading Lb. COD/ Lb. Carbon Average
First Rains	377	67	0.23
Second Rains	233	48	0.26

As noted previously, problems with varying feed COD and algae growth were experienced during some of the runs. These problems undoubtedly limited the performance to poorer levels than could have been attained under ideal steady state conditions. However, these are the real problems that exist when treating refinery waste waters and we therefore feel the carbon loadings attained are indicative of the true performance of the commercial plant.

CARBON HANDLING AND REGENERATION

This system is shown in Figure 5. The spent carbon is removed as a water slurry through a carbon removal trough and nozzle even with the top of the gravel layer. The slurry flows by gravity and with the aid of water jets in the carbon removal trough to the spent carbon transfer pump sump. From here a rubber lined pump transports the carbon slurry into the spent carbon tank. The tank has capacity to contain the contents of one cell. From this tank the carbon is educted with high pressure water to the dewatering screw above the regeneration furnace. A timer valve on the spent carbon line feeding the eductor opens and closes at timed intervals to allow close control of the carbon flow to the regeneration furnace. The dewatering screw separates most of the water from the spent carbon slurry and the drained water is returned to the reservoir. The carbon discharging into the furnace contains approximately 50 per cent by weight of water.

The regeneration furnace is a 56" I.D. multiple hearth type with a total of six hearths. It is gas fired and internal temperatures are controlled to about 1600°F. A center shaft with rabble arms moves the carbon across each hearth and downward through the furnace. An elaborate flue gas quench and scrubber system is installed to meet local Air Pollution Control District requirements. The furnace is designed to regenerate 8,000 pounds of carbon per day or one bed in about 6 to 7 days.

The regenerated carbon drops into a quench tank just below the furnace from where it is educted into the regenerated carbon tank. From this tank the carbon is then educted and transported through a hose back to the same cell where it originated.

The carbon handling system has worked very well. The original 1" cast iron eductors were too small and soon lost capacity due to erosion. Larger stainless steel eductors and a reduction of motive water pressure from 110 psig to 50 psig have remedied this. Also originally we had some problem with displaced support gravel from the bottom of the cells plugging up the eductors. This was remedied by constructing a gravel screen in the top of the spent carbon tank to remove the gravel. The time required to transfer the carbon out of the cell to the spent carbon tank is about 14 hours while transfer back to the cell from the regenerated carbon tank takes about 7 hours.

Operation of the regeneration furnace has been excellent. The major effort relative to this operation has been to develop a reliable method for determination of the quality of the regenerated carbon. After operational guidelines were developed, the furnace consistently regenerated the spent carbon to near virgin activity.

Our experience indicates that about a 5 per cent loss is incurred during carbon handling and the regeneration. We feel the majority of this is due to attrition of the carbon and resulting production of fines. These fines are backwashed out of the cells prior to being placed in operation and end up back in the reservoir where they settle out.

OPERATING COSTS

Actual operating costs for the second year of operation are shown in Table 3.

Cost Data
December, 1972 - March, 1973
Table 3

Cost Areas	Cents Per Thousand Gallons of Water Treated	Cents Per Pound of COD Removed
Utilities	9	4
Repair Labor	3	1
Operating Labor	15	7
Carbon	11	5
Miscellaneous	2	1
Total	40	18

Updating these costs to 1976 levels would give about 56 cents per thousand gallons of water treated, or about 25 cents per pound of COD removed.

CONCLUSIONS

The plant has proved to be easy to maintain, easy and quick to start up, simple to shut down and leave in a standby stage, and very reliable in its performance.

For the unique intermittent type operation required at the Watson Refinery, we feel the Carbon Adsorption Process has been successful. However, we do not feel that this conclusion would necessarily be the same for a continuous operation requirement or some other unique situation.

DISCUSSION

Gantz: Did you experience any solids handling problems?

M. A. Prosche: We had no solid handling problems. We had some concern about the silt, sand, and carbon fines building up in the bottom of the reservoir. But during the summer months we just moved in a front-end loader and removed all solids.

Ben Buchanan: I was wondering what control methods you used on your reactivation furnace to control the reactivation.

M. A. Prosche: What we finally did was measure the ABD, apparent bulk density, of the carbon being fed to the furnace and the regenerated carbon from the furnace. We found that a reduction of gm/cc in ABD was sufficient to bring the carbon back up to 100% adsorption efficiency. In actual practice the operators had a pre-weighed cube and a balance at the unit. The cube was then used to weigh a fixed volume of feed and product carbon and the difference used as the guide to furnace operation. As a generality, spent carbon had an ABD of 0.56 gm/cc and the regenerated 0.50 gm/cc.

Ben Buchanan: How did you determine how much of your carbon was lost by attrition, and how much was lost through burning in your regeneration furnace?

M. A. Prosche: The only insight we had was to roughly know how much carbon we put back into the cells after regeneration, and the amount of carbon that had accumulated in the bottom of the reservoir after a season of operation. It appeared to us that the accumulated fines in the reservoir about equaled the loss in volume in the beds.

Ben Buchanan: There is a little problem with measuring volumes because I think the losses that you have from burning the carbon do not necessarily reduce the size but many of those losses are inside the particle and do not show up. You will get a weight loss but you do not necessarily get the same volume loss.

M. A. Prosche: That could very well be. This was not a research project but strictly a demonstration project to determine feasibility and costs.

Larry Echelberger: Has there been any attempt to reuse this water in your refinery after you clean it up? Is it high in TDS? Do you attempt to reuse the water at all?

M. A. Prosche: The discharge is primarily refinery waste water diluted with rain water. The waste water consists of untreated service water, desalter waters, and water from tank bottoms. So this water would require extensive pretreatment prior to any reuse. Our primary thrust now is to reuse stripped sour water which is essentially contaminated consensate. Following the successful utilization of all of this water, we can then turn our attention to the more difficult problems of reusing the waste water.

BIOGRAPHY

Marvin A. Prosche is Manager of Refinery Technology at Atlantic Richfield's Watson Refinery. He holds a B.S. in ChE from the University of Notre Dame and an M.S. in ChE from the University of Illinois. His experience includes 25 years of petroleum refinery process design and process engineering.

FIGURE 1

WASTE WATER ACTIVATED CARBON TREATMENT PLANT

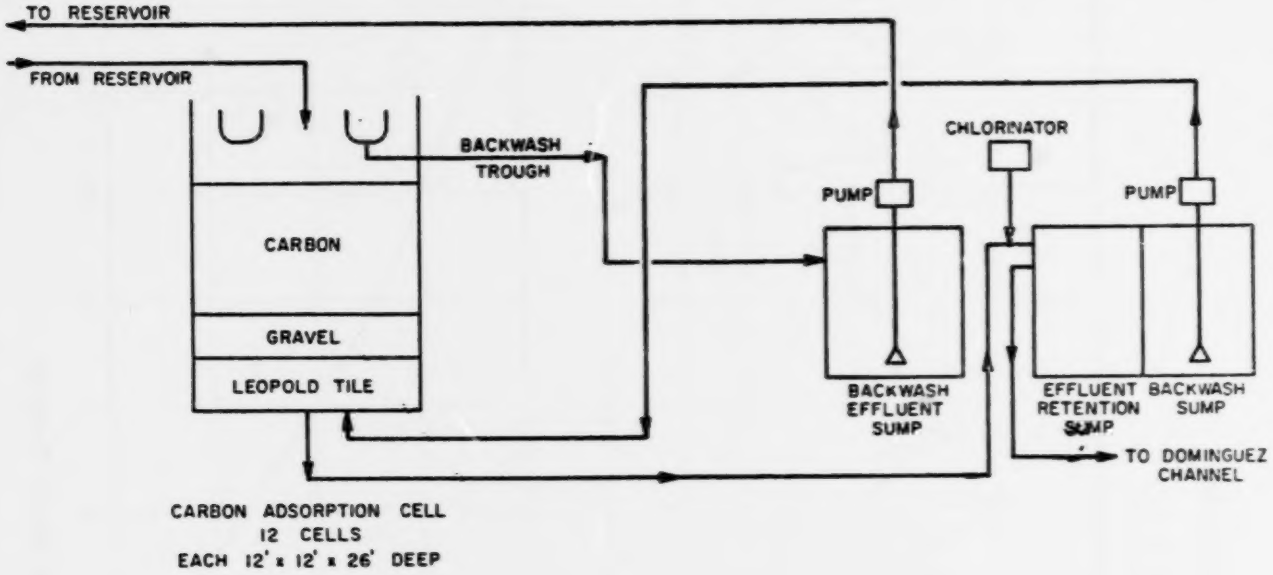
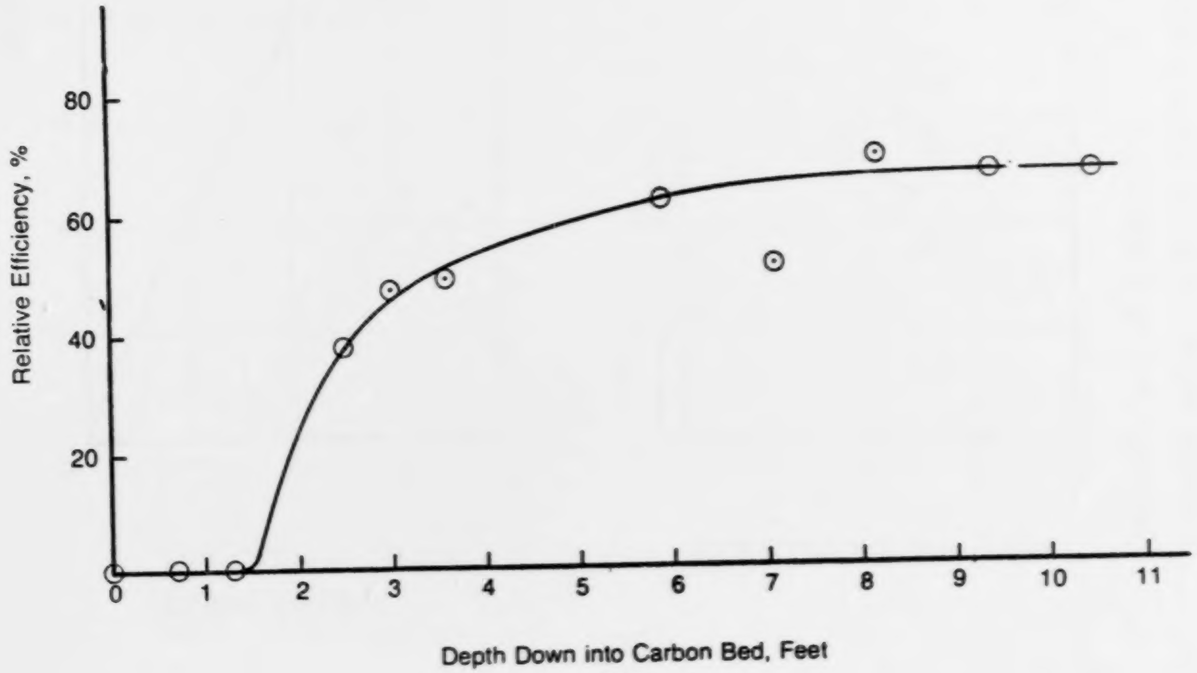

TO RESERVOIR
FROM RESERVOIR
BACKWASH TROUGH
CARBON
GRAVEL
LEOPOLD TILE
CHLORINATOR
PUMP
PUMP
BACKWASH EFFLUENT SUMP
EFFLUENT RETENTION SUMP
BACKWASH SUMP
TO DOMINGUEZ CHANNEL
CARBON ADSORPTION CELL
12 CELLS
EACH 12' x 12' x 26' DEEP

Figure 2

Relative Efficiency Profile of Cell
After 208 Hours of Operation @ 250 GPM and
650 to 600 PPM COD in Feed



Typical Performance Data—Staggered Operation
Second Rainy Season

Figure 3

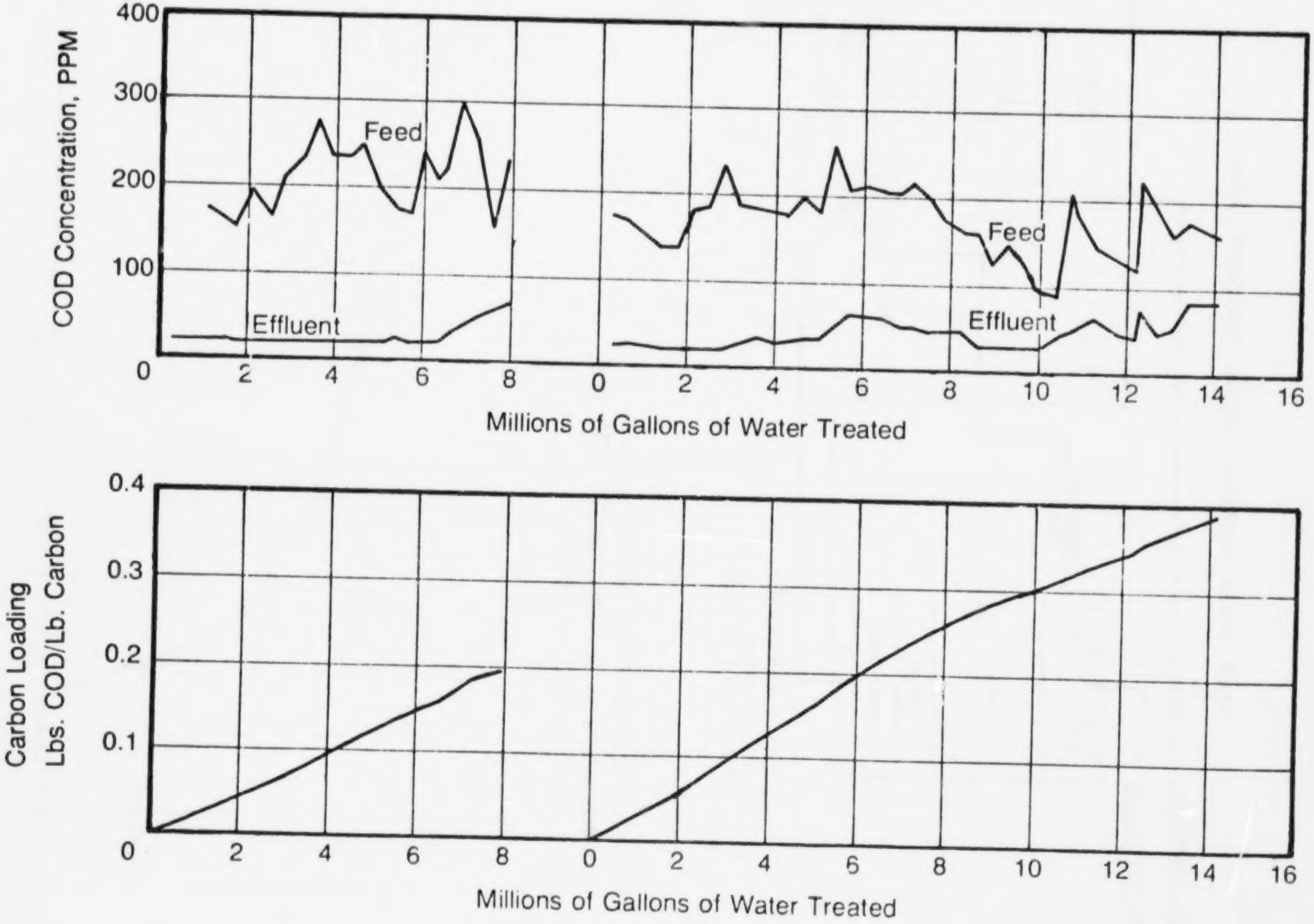


Figure 4

Performance Data—Bulk Processing Cells
Second Rainy Season

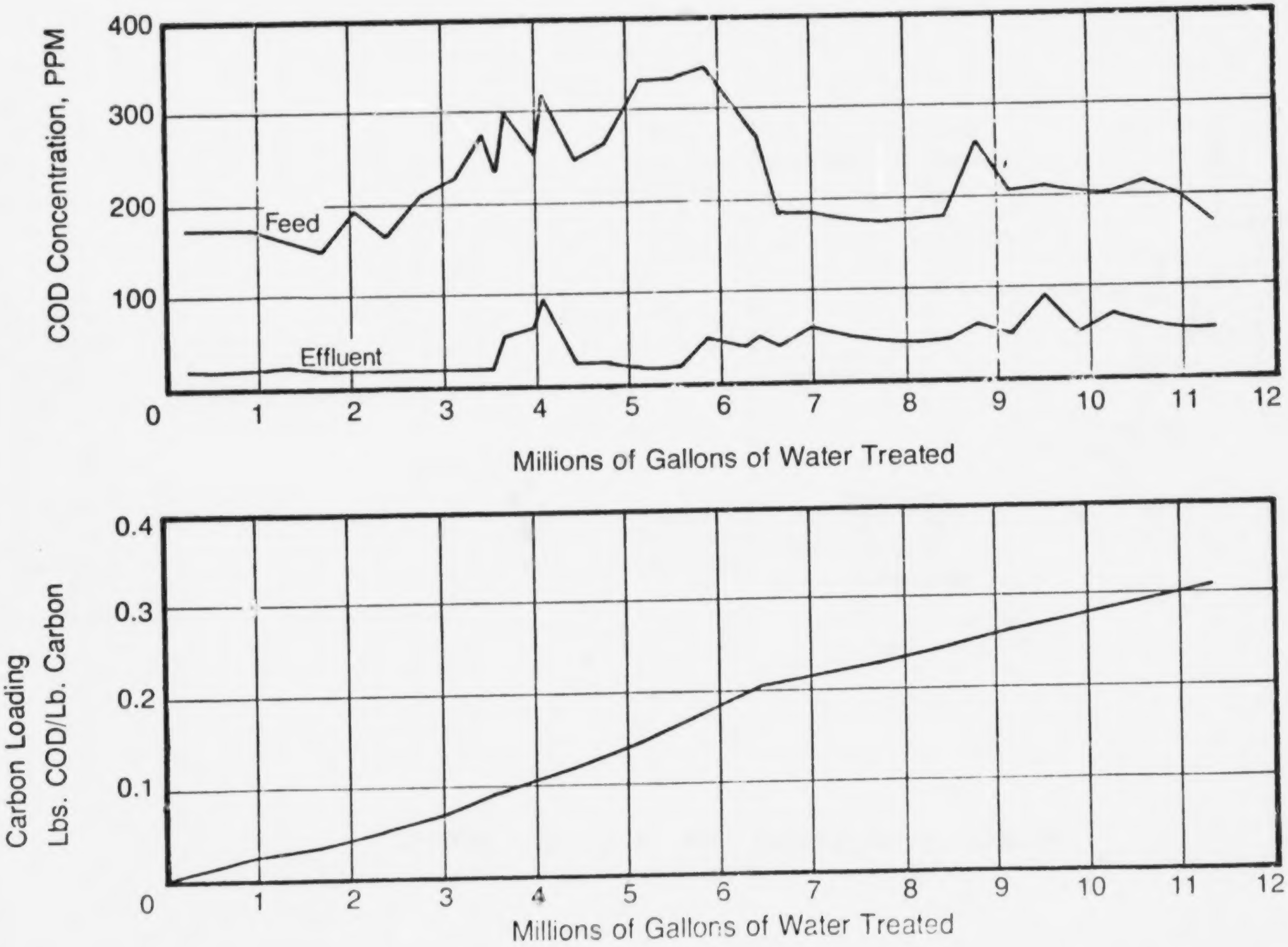
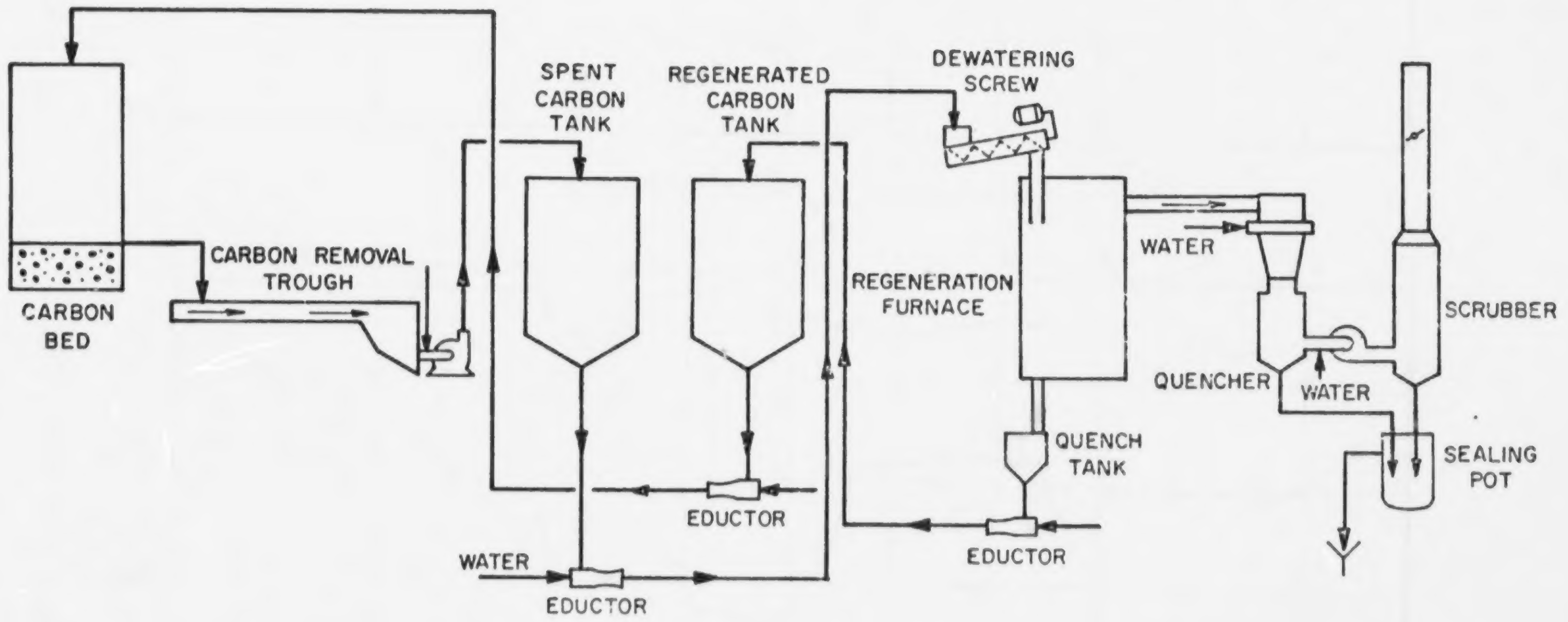


FIGURE 5

CARBON TRANSFER AND REGENERATION SYSTEM


CARBON BED
CARBON REMOVAL TROUGH
SPENT CARBON TANK
REGENERATED CARBON TANK
WATER
EDUCTOR
EDUCTOR
DEWATERING SCREW
REGENERATION FURNACE
QUENCH TANK
EDUCTOR
WATER
QUENCHER
WATER
SCRUBBER
SEALING POT

SESSION VI

"MISCELLANEOUS TOPICS"

Chairman

M.K. "Don" Hutton

Manager, Mechanical and Environmental Engineering
Kerr-McGee Refining Corporation
Oklahoma City, Oklahoma

Speakers

Lial F. Tischler

"Inherent Variability in Wastewater Treatment"

R.T. Milligan

"Reuse of Refinery Wastewater"

Sterling L. Burks

"Biological Monitoring of Petroleum Refinery Effluents"

Ronald G. Gantz

"API - Sour Water Stripper Studies"

WATER POLLUTION ABATEMENT AT BP OIL CORPORATION'S MARCUS HOOK REFINERY

B. A. McCrodden*

ABSTRACT

BP Oil Corporation's Marcus Hook Refinery has achieved first stage ultimate oxygen demand standards prescribed by the Delaware River Basin Commission by operating a wastewater treatment system consisting of rapid sand filtration, for removal of oil and suspended solids, followed by granular activated carbon adsorption, for removal of dissolved organic material. Associated equipment includes backwash holding tanks, sludge thickeners, two-stage centrifugation for oil-water-sludge separation, and a multiple hearth furnace for carbon regeneration.

The 2.2 MGD Wastewater Treatment Plant has demonstrated average removals by the rapid sand filters of 67, 67, and 20 percent reduction for oil, suspended solids, and first stage ultimate oxygen demand respectively. Average removals by the activated carbon adsorbers have been 74, 40, 27, 49, and 99 percent reduction for oil, suspended solids, first stage ultimate oxygen demand (FSUOD), chemical oxygen demand, and phenol respectively.

Capital cost of the Wastewater Treatment Plant, constructed on a one-quarter plot, was $1,822,000, with a projected annual operating cost of $183,000.

INTRODUCTION

A 2.2 MGD sand-filtration-activated carbon adsorption Wastewater Treatment Plant, placed in operation at the Marcus Hook Refinery of BP Oil Corporation, a subsiderary of the Standard Oil Company (Ohio), in March, 1973, has demonstrated overall removals of 80, 92, 42, 64, and 99 percent reduction for suspended solids, oil, first stage ultimate oxygen demand (FSUOD), chemical oxygen demand (COD),and phenol respectively.

The 105,000 BPD Class B Refinery, located in southeastern Pennsylvania, discharges its effluent waters into the Delaware River. In 1961, the Delaware Estuary became the subject of an intensive study by the then U.S. Public Health Service. The Delaware Estuary Comprehensive Study (DECS) served as a basis for a determination by the Delaware River Basin Commission (DRBC) that the 1964 discharge loads to the Estuary exceeded its assimilative capacity. Subsequently, stream quality objectives were established and the Estuary divided into six zones. The total first stage ulimate oxygen demand permitted to be discharged without violating these objectives was determined for each zone from base data developed by the DECS and its application of a mathematical model. Under the doctrine of equitable apportionment, each individual discharger to a zone received an allocation based upon the concept of equal percentage of raw waste reduction in that zone. The Refinery's measured raw waste load was 24,650 pounds per day FSUOD. Application of an 89.25 zone percent reduction lead to an overall discharge allocation of 2650 pounds per day FSUOD. This allocation includes the net contribution from the process wastewater and once through cooling water streams.

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*Conservation Engineer, BP Oil Corporation

An additional Delaware River Basin Commission requirement is the secondary treatment of all process wastewater streams. Secondary treatment for zone four of the Estuary is defined as 89.25 percent FSUOD reduction.

In 1969 a compliance schedule of 48 months was established. The initial effort toward achieving compliance was the evaluation of the existing API oil-water-solids Separator, through which all process wastewater flow is directed. Monitoring of API Separator influent and effluent FSUOD determined an average 68 percent removal, far below the DRBC's required 89.25 percent for process wastewater streams. Accordingly, a project to determine the treatability of the API Separator effluent, and a project to reduce the API Separator's hydraulic loading were undertaken. The latter project had as its basis an in-plant water use survey which concluded that a reduction on process wastewater flow to the API Separator could be accomplished by installation of a brine cooler; replacement of barometric condensers with surface condensers; segregation of sanitary wastes from the process wastewater stream; and further segregation of this project are evidenced by a reduction in the hydraulic loading from 3750 to 1450 GPM.

Treatability of the API Separator effluent was investigated through the operation of a bench-scale sludge unit and an extended aeration pilot plant. With accumulated data as the basis, a preliminary biological treatment system design was prepared. The proposed full-scale design required intermediate facilities for oil removal, two 369,000 gallon aeration basins, final clarifiers, an anaerobic digester, and both biological and oily sludge dewatering facilities.

Review of an estimated biological treatment capital cost of $2,500,000; an estimated annual operating cost of $220,500; biological treatment variability; land requirements; and excess sludge generation, led to investigation of a sand filtration-activated carbon adsorption treatment system.

Bench-scale single media filtration of API Separator effluent resulted in an outlet of acceptable quality for feed to an activated carbon contactor. An adsorption isotherm, presented as Figure 1, was prepared using filtered water and indicated a theoretical loading of 0.3 gm of TOC adsorbed per gram of carbon. This is equivalent to one pound of carbon exhausted per 1000 gallons of wastewater treated.

Based on the above results, operation of a sand filtration pilot plant followed in line by a dynamic carbon column test was continued for a six week period to establish design parameters.

Filtration rates ranging from 12-18 GPM/sq. ft resulted in average removals of 79, 77, and 35 percent reduction for oil, suspended solids and FSUOD respectively. Average removals by activated carbon adsorption were 85, 62, 83, 65, and 99 percent reduction for oil, suspended solids, FSUOD, TOC, and phenol respectively as shown in Table 1. Projection of the carbon column test data indicated an exhaustion rate of 0.86 pounds of carbon per 1000 gallons of throughput.

With accumulated data as the basis, a preliminary sand filtration-activated carbon adsorption design was prepared. Comparison of an estimated capital cost of $2,000,000; an estimated annual operating cost of $179,000; and reduced land area requirements, with biological treatment preliminary design, led to the decision to commence filtration-adsorption design. Figure 1A presents a schematic flow diagram of the treatment facilities designed.

SAND FILTRATION DESIGN

Three parallel rapid sand filters were designed to remove oil and suspended solids from the API Separator effluent. Design removals were those achieved during pilot operation. An intermediate basin was included in the design to control flow surges and equalize influent overloads.

Each filter is 10 feet in diameter by eighteen feet six inches overall height. Flow enters the bottom of the vessel and rises vertically through a 10 inch pipe in the center of the filter. A rated flow of 1000 GPM per filter corresponds to a superficial hydraulic loading of 12.8 GPM/ft.^{2}

Flow to the filter system is controlled by a level controller which maintains a constant level in the intermediate surge basin. The effluent flow from each filter is sensed by individual flow indicators. The flows are summed and equally divided among the three filters by throttling each filter's effluent control valve.

Under normal filtering conditions the vessel is full of water to the vent connection on top. The water flow is down through the filter media of 2.5 feet of anthracite and 4.5 feet of sand; through the support gravel; and through the nozzles which are inserted in a tube sheet. The water beneath the tube sheet flows out through the outlet connection to a 30,000 gallon filtered water holding tank.

Removal of suspended solids and oil trapped by the filters is accomplished by backwashing with water stored in the filtered water holding tank.

The initial step in backwash is to remove the water remaining in the filter by applying air pressure to the top of the vessle. This allows an up flow air and water scour to follow and effectively remove adhering suspended solids and oil from the sand and anthracite particles. Scour rates are 7.1 GPM/ft.^{2} and 7.1 SCFM/ft.^{2} As the scour water reaches the top of the vessel, the air is shut off and the water rate increases to 25.1 GPM/ft.^{2}, thereby flushing the filter of trapped suspended solids and oil. The backwash water overflows into the center standpipe and is directed to a 30,000 gallon sludge blending tank.

The backwash cycle is automatically operated by a Programmed Timer which can be initiated by an interval timer, high differential pressure, or manually by pushbotton. The three filter system is designed to allow only one filter to backwash at any one time. The filters will automatically backwash in numerical sequence. Although the filters were designed to operate with one off-line, the mode of operation is to have an individual filter off-line only during its backwash cycle. If the level in the filtered water holding tank is low or the level in the sludge blending tank is high, the backwash cycle cannot proceed and an alarm is annunciated.

Table 11 summarizes the rapid sand filter design data.

ACTIVATED CARBON ADSORPTION DESIGN

Three parallel activated carbon adsorbers were designed to remove soluble organic matter from the sand filter effluent at a maximum flow rate of 2000 GPM. Design removals were those obtained during pilot operation.

Each adsorber is a carbon steel vessel 10 feet in diameter by 65 feet overall height and is lined with 12-15 mils of

Plastite. The adsorbers each contain 92,000 pounds of granular activated carbon in a bed depth of 45 feet. An additional 8000 pounds of carbon occupies the upper and lower end cone areas. The upper and lower cone angles are 90 and 46 degrees respectively, based on the angle of repose of granular activated carbon immersed in water.

Flow to the three adsorbers is controlled by the level in the filtered water holding tank, which acts as a feed surge basin. The influent to each adsorber is distributed through a circumferential manifold located just above the lower cone section. The flow is directed downward under an internal cone, then upward through a 3 foot diameter opening in the internal cone. A design flow to each adsorber of 667 GPM corresponds to an empty bed contact time of 40 minutes.

The upward flow through the packed bed at a superficial hydraulic loading of 8.5 GPM/ft.^{2}, is discharged through eight internal septums which extend vertically from the upper cone. The septums are stainless steel well screens which retain the 1.5 mm diameter activated carbon particles in the adsorber. Filtered service water is provided at each septum for backflushing, should plugging due to carbon fines occur.

Continuous adsorption is dependent upon the removal of exhausted carbon from the adsorbers and the addition of regenerated carbon. One thousand pounds per day of spent carbon is pulsed from each of the three adsorbers. During the pulse period, which occurs for each vessel every 24 hours, the adsorber is taken out of service. The hydrostatic pressure available at the lower cone apex is used to transport the carbon slurry to a flooded collection tank. A pulse period of 1.4 seconds allows the desired 1000 pounds of carbon to be transferred under velocities of 5 feet per second. Transfer lines are 4 inch schedule 40 carbon steel with schedule 80 long radius sweeps. Ball valves are used in carbon slurry service. During this pulse period, regenerated carbon is added to the top of the adsorber from a carbon storage tank located above each vessel.

As the ball valve at the adsorber apex closes to stop spent carbon flow, filtered service water is introduced to flush the line, thereby preventing carbon bridging. Freezing problems are avoided by draining the transfer line following completion of the water flush.

A cone bottom carbon collection tank receives the spent carbon and acts as the regeneration furnace feed tank. A ball valve at the apex of the collection tank pulses carbon for 8 seconds into a dewatering screw at two minute intervals. Filtered water is added at the apex to prevent carbon bridging, and is added to the dewatering screw to further wash the carbon of free oil which was "filtered out" in the adsorber. Overflows from the collection tank and dewatering screw are directed to a carbon settler from which the carbon is ejected into the dewatering screw and the water overflows to be reprocessed.

Table III summarizes the activated carbon adsorption design data.

THERMAL REGENERATION DESIGN

A five foot diameter multiple hearth furnace was designed to thermally regenerate the spent carbon. The dewatered carbon enters the six hearth furnace through an 8 inch inlet for regeneration at a design rate of 125 pounds per hour. The carbon is moved downward through the fire brick lined hearths by stainless steel rabble arms. In the first hearth, which is unfired but maintains a temperature of 1100°F., any remaining moisture is vaporized. Hearths four and six, numbered from the top, are tangentially fired by two burners using refinery fuel gas at rates of 188 and 68 CFH respectively, to maintain respective temperatures at 1725°F. and 1750°F.

In an atmosphere controlled by addition of steam at a design rate of 125 pounds per hour, the adsorbed organics are volatilized and oxidized. To assure complete oxidation, all flue gases pass through an integral afterburner fired by refinery fuel gas and maintained at a temperature of 1250°F. Recirculation of shaft cooling air provides sufficient oxygen for combustion. Prior to emission to the atmosphere, the flue gases pass through a two foot diameter, four plate, Impinjet wet scrubber using filtered service water for gas cooling and particulate removal to 0.04 grains per standard cubic foot (dry).

Temperature indicator controllers maintain the desired temperature in the fired hearths. Furnace safety features include ultra-violet flame scanners which cause an alarm to annunciate should the combustion air blower, induced draft fan, or the shaft cooling air fan fail. Abnormally high or low fuel gas pressure will cause the main gas safety valve to close, resulting in a flame-out at all burners.

Regenerated carbon is discharged from the furnace into a 12 cubic foot cone bottom quench tank flooded with filtered service water. Temperature reduction, the addition of make-up carbon, and the formation of a carbon slurry occur in the quench tank. As the carbon level in the quench tank increases a rotating bindicator is stopped and a timed sequence is initiated to transfer the regenerated carbon to one of three 96 cubic foot carbon storage tanks located above each adsorber.

During the time controlled sequence, the carbon slurry flows by gravity into a 5 cubic foot blow case. Filtered service water is then introduced into the blow case to pressure the carbon at velocities of 5 feet per second through 2 inch transfer lines of schedule 40 carbon steel with schedule 80 long radius sweeps. The slurry transfer is followed by a water flush and an air drain to clear the line. In the event a high level is indicated by a storage tank bindicator, the carbon is automatically transferred to the next storage tank.

Carbon addition to the adsorbers from the storage tanks, which occurs during the pulsing of spent carbon from the bottom cone, is judged complete by a bindicator located in the upper cone. Should the bindicator indicate a low level, the adsorber may not be brought back into service.

An additional safety feature is an atmospheric vent from the top of the adsorber to its carbon collection tank. In the event a number of septums plug simultaneously, excess flow will be vented, and overflow the collection tank to the carbon settler. A pressure gage is located on the vent line to indicate such an occurance.

Table IV summarizes the regeneration furnace design data.

SOLIDS DEWATERING SYSTEM DESIGN

A solids handling system was designed to separate the sludge removed at the Sand Filters, API Separator, and Emulsion Treater into an oil, water, and solid phase. Upon separation, the oil is recovered, the water is returned for reprocessing, and the solids are disposed on a sanitary landfill.

The three intermitent sludge streams noted above are mixed in a 30,000 gallon sludge blending tank and transferred to a 26,000 gallon circular thickener at a rate of 60 GPM. The design loading of 30 pounds per square foot per day results in an underflow concentration of 2.5 percent solids. The thickener underflow of 20 gallons per minute and overflow of 40 gallons per minute are directed to the sludge holding tank and API Separator respectively. Should an emulsion layer accumulate on the thickener, it is skimmed directly to the sludge holding tank. The sludge holding tank acts as a feed surge basin for the scroll centrifuge.

Feed the scroll centrifuge, flowing at 20 GPM, passes through a double pipe heat exchanger which maintains an outlet temperature of 150°F. Operating at 2600 RPM, the scroll centrifuge discharges a stream of 50 percent solids, and an oil-water stream. The solids are carried by conveyor belt to a holding container to await disposal. The liquid centrate is directed to the disc centrifuge feed sump.

The disc centrifuge feed, at 20 GPM, passes through a double pipe heat exchanger which maintains an outlet temperature of 180°F. An additional 25 GPM of filtered service water also enters the disc machine at 180°F. to establish a nozzle seal. Operating at 6350 RPM, the disc centrifuge discharges an oil stream for recovery, a water stream for reprocessing, and a solids-water stream, also for reprocessing through the API Separator.

SAND FILTER PERFORMANCE

The three parallel rapid sand filters have demonstrated average removals of 67, 67, and 20 percent for oil, suspended solids, and FSUOD respectively. The average influent flow of 1795 GPM corresponds to an average superficial hydraulic loading of 7.8 GPM/ft/^{2}.

The original design mode of operation has been revised to permit all filters to equally divide the flow, rather than have two filters in-service and one off-line, thus the lower average superficial hydraulic loading noted above. With the current mode of operation, an individual filter is only off-line during a backwash cycle.

Analysis of the data presented in Table V indicates average removals of 6.6, 4.6, and 2.1 lbs./D/ft.^{2}. for oil, suspended solids, and FSUOD respectively. The units of pounds per day per square foot, represents a simultaneous evaluation of concentration and hydraulic loadings.

Table VI presents an analyses of sand filter backwash water. Based on this data the backwash high rate flush duration was increased to 7 minutes and the flow rate was increased to greater than 2000 GPM. The total backwash duration averages 20 minutes and is dependent upon the time required for the pressurized removal of water remaining in the filter. The time required is a function of the differential pressure across the sand filter when a backwash is initiated. The backwash interval is currently set at 3.5 hours, ie,. each individual filter is backwashed every 10.5 hours.

Although the design included a differential pressure override to initiate backwash, this option is not currently utilized since the maximum differential pressure reached during the above backwash interval has been 3 PSI.

To date the factor limiting the backwash interval has been the capacity of the sludge blending tank which receives backwash water.

An operating problem encountered has been a decrease in effluent quality due to a backwash cycle. The two filters remaining on line experience a "shock" as the individual flow rates increase to include the portion of flow previously handled by the third filter. The decrease in effluent quality was due to the expelling of suspended solids trapped in the filter, and the decrease in suspended solids removal at the increased superficial hydraulic loading. An increase in effluent quality was obtained by setting the controls to maintain the established flow rate to each on-line filter during a backwash cycle.

A decrease in effluent quality was also observed during the removal of water remaining in the filter by applying air pressure print to backwash. Table VII presents an analyses of this water and indicates that suspended solids are removed from the filter and contaminate the effluent water stored in the filtered water holding tank.

The installation of drain lines to direct this water removed from the sand filter to the API Separator is expected to result in an increase in filtered water quality.

ACTIVATED CARBON ADSORPTION PERFORMANCE

The three parallel activated carbon adsorbers have demonstrated average removals of 74, 40, 27, 49, and 99 percent for oil, suspended solids, FSUOD, COD, and phenols respectively. The average influent flow of 1450 GPM corresponds to an empty bed contact time of 55 minutes. The average superficial hydraulic loading experienced has been 6.2 GPM/ft.^{2}.

The 345 GPM difference between filter and adsorber flow is due to the utilization of filtered water as unit service water and as backwash water.

Table V prese ts adsorber influent and influent data. Review of this data must consider the operating period duration, especially with respect to the carbon detention period of 92 days in the adsorber bed since the data was obtained during a period when a portion of the bed was esentially virgin carbon.

The carbon adsorbers utilize the removal merchanisms of adsorption, filtration, and biological degradation.

During initial operation, the adsorbers were receiving an influent containing 1 ppm of dissolved oxygen, and discharging an influent containing zero dissolved oxygen. The occurance of anerobic digestion in the adsorbers was indicated by an increase in sulfide concentration from an influent of 0.6 ppm to an effluent of 13.4 ppm. The influent concentration of organic sulfur compounds was determined to be 0.01 ppm. Further investigation of the effluent odor problem due to the sulfide produced in the adsorbers indicated the presence of butyl mercaptan, tiophene, and dimenthal sulfide in the adsorber effluent.

In order to correct the effluent odor problem, air was injected into the sand filter effluent manifold and an increase was obtained in the adsorber influent dissolved oxygen concentration to 3.0 ppm. The average decrease in dissolved oxygen though the adsorbers has been 93 percent, leaving an effluent dissolved oxygen residual of 0.2 ppm. Although activated carbon has an affinity for oxygen, a 15 percent increase in ammonia concentration through the adsorbers indicates that biological activity is occurring. The detection of dissolved oxygen in the effluent and a significant reduction in the odor problem have occurred, however, an increase in sulfide concentration to an average of 7 ppm is indicative of continuing anaerobic digestion. In order to maintain aerobic conditions and eliminate the sulfide production, injection of hydrogen peroxide will be evaluated with respect to its effect on sulfide production, dissolved oxygen concentration, flow rate, and phenol, BOD, and COD removals.

The average TOC loading on the spent carbon removed from the adsorbers has been 0.22 pounds TOC/pound carbon. The average COD loading has been 0.42 pounds COD/pound carbon while the phenol loadings experienced have been 0.09 pounds phenol/pound carbon.

The low phenol loading lead to an increase in effluent phenol concentrations following introduction of 100 GPM of Foul Condensate Stripper bottons containing an average 300 ppm phenol. The increased effluent phenol concentrations noted in Table V are a result of the spent carbon wave front moving toward through the carbon bed. In order to achieve design removals, the carbon regeneration rate was increased to 250 pounds per hour, thereby providing additional adsorptive capacity.

It was observed that during the period in which the spent carbon wave front had moved upward in the adsorber, the increase in phenol effluent concentration occurred at low adsorber influent values. This was a result of the adsorbed phenol achieving equilibrium with the phenol in solution in the wastewater. Again, lowering the spent carbon wave front will provide additional adsorptive capacity and eliminate the occurrence of this phenomenon.

An operating problem encountered has been the decrease in effluent quality due to the pulsing of spent carbon from an off-line adsorber. The two adsorbers remaining on-line experience a "shock" as the individual established flow rates increase to include that portion of flow previously handled by the third adsorber. The decrease in effluent quality was due to the expelling of oil and carbon fines from the adsorber. A similar expelling occurs from the third adsorber as flow is restored. In order to reduce the "shock" to the carbon bed, the time required to open and close the adsorber influent valve will be set to maintain the established flow rate to each on-stream adsrober during the carbon pulse cycle.

A second problem encountered has been the inability to achieve the design maximum flow rate of 2000 GPM through the adsorbers. Entrapped suspended solids, oil, and carbon fines contribute to an excessive pressure drop through the bed. Following an individual bed pulse, an increase in the maximum flow rate to the adsorber is observed. Currently, the pulsing and regeneration rate has been increased to remove the entrapped matter and virgin fines in an attempt to achieve the design flow rate. Flushing the adsorbers has also been successful in obtaining an increased flow rate. The flush is accomplished by closing the adsorber effluent valves and introducing 150 GPM into the base of the vessel and allowing the bed to expand into the carbon storage tank above the adsorber. The flush water containing carbon fines overflows the carbon storage tank to the carbon settler, from which the water is directed to the API Separator and the settled carbon fines are transferred to the regeneration furnace where they are combusted.

THERMAL REGENERATION PERFORMANCE

Spent carbon regeneration has been achieved using a six-hearth furnace fired by refinery fuel gas.

Regeneration at the 3000 pound/day rate is controlled by measurement of the regenerated carbon apparent density and comparing the value with virgin carbon. To date, the average density of regenerated carbon has been 49.1 g/100cc, which compared with a virgin carbon value of 45.1 g/100cc. Changing the atmosphere in the regeneration furnace by varying the amount of steam injected has been the method used to control the carbon density. The current steam addition rate is 30 LB./HR. A decrease in steam addition was found to allow additional combustion of adsorbed materials and thereby decrease the carbon density.

Adsorption isotherms prepared for both regenerated and spent carbon were equivalent indicating regeneration tothe carbon's adsorptive capacity was achieved.

Carbon losses to date have been 10 percent per regeneration cycle. This high loss value may be attributed to mechanical and start-up problems rather than to excessive carbon attrition, and is expected to approach the design 5 percent loss as equipment modifications are completed. These modifications include the installation of a surge tank associated with the spent carbon collection tank and revisions to the carbon settler to increase its capacity.

SOLIDS DEWATERING SYSTEM PERFORMANCE

An analytical evaluation of the solids dewatering system has not been performed to date. Operating problems encountered resulted in an extended shutdown of the disc centrifuge and the inability to accept API Separator and Emulsion Treater sludges.

Revisions to the disc centrifuge systems will be completed to provide flow control of the feed at 20 GPM, replacing the existing level controlled mode of operation. In addition, the sealing water will be flow controlled at 25 GPM to prevent the flushing of bearing grease which occurred previously, causing a bearing burnout and resulted in the extended shutdown.

Sludges from the API Separator and Emulsion Treater caused severe plugging problems in the solids dewatering system. The inlet screens at the sludge blending tank, three inch transfer lines, pump impellers, and the double pipe heat exchangers experienced plugging due to the debris contained in these sludges. The problem has been corrected by installing a comminutor prior ro the in-line centrifugal pump that transfers sludge from the blending tank to the thickener.

Extended operation at design conditions will permit evaluation of the centrifuge system.

ECONOMIC EVALUATIONS

Tables VIII and IX present Wastewater Treatment Plant capital and annual operating costs totaling $1,822,400 and $183,000 respectively.

The estimated annual operating cost is presented due to the current operating period during which labor, maintenance, and carbon addition were not representative of normal operating conditions.

Considering equipment life to be 10 years, and the cost of capital 35%, Wastewater Treatment Plant unit costs, including filtration adsorption and solids dewatering, are 24¢/1000 gals. capital and 7¢/1000 gals. operating.

SUMMARY

Treatment of the Marcus Hook Refinery's process wastewater using sand filtration and activated carbon adsorption has produced an effluent acceptable for discharge to the Delaware River.

Extended operation will permit further evaluation of this application of a filtration-adsorption wastewater treatment system.

CREDITS

This project was supported in part by Demonstration Grant No. 12050GXF from the Research and Monitoring Division of the U.S. Environmental Protection Agency.

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MARCUS HOOK, PENNSYLVANIA

CARBON ADSORPTION ISOTHERM OF FILTERED WASTEWATER

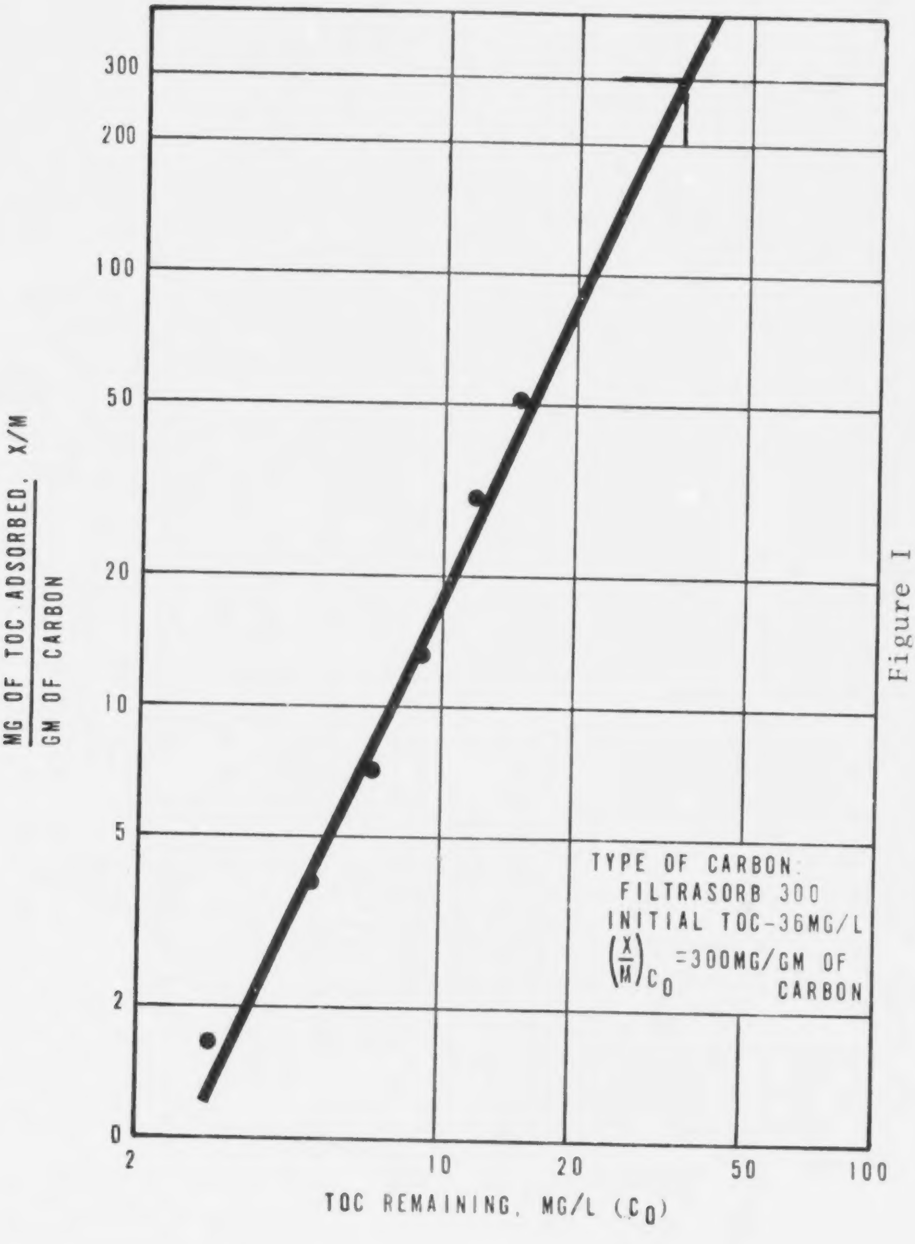

Figure I

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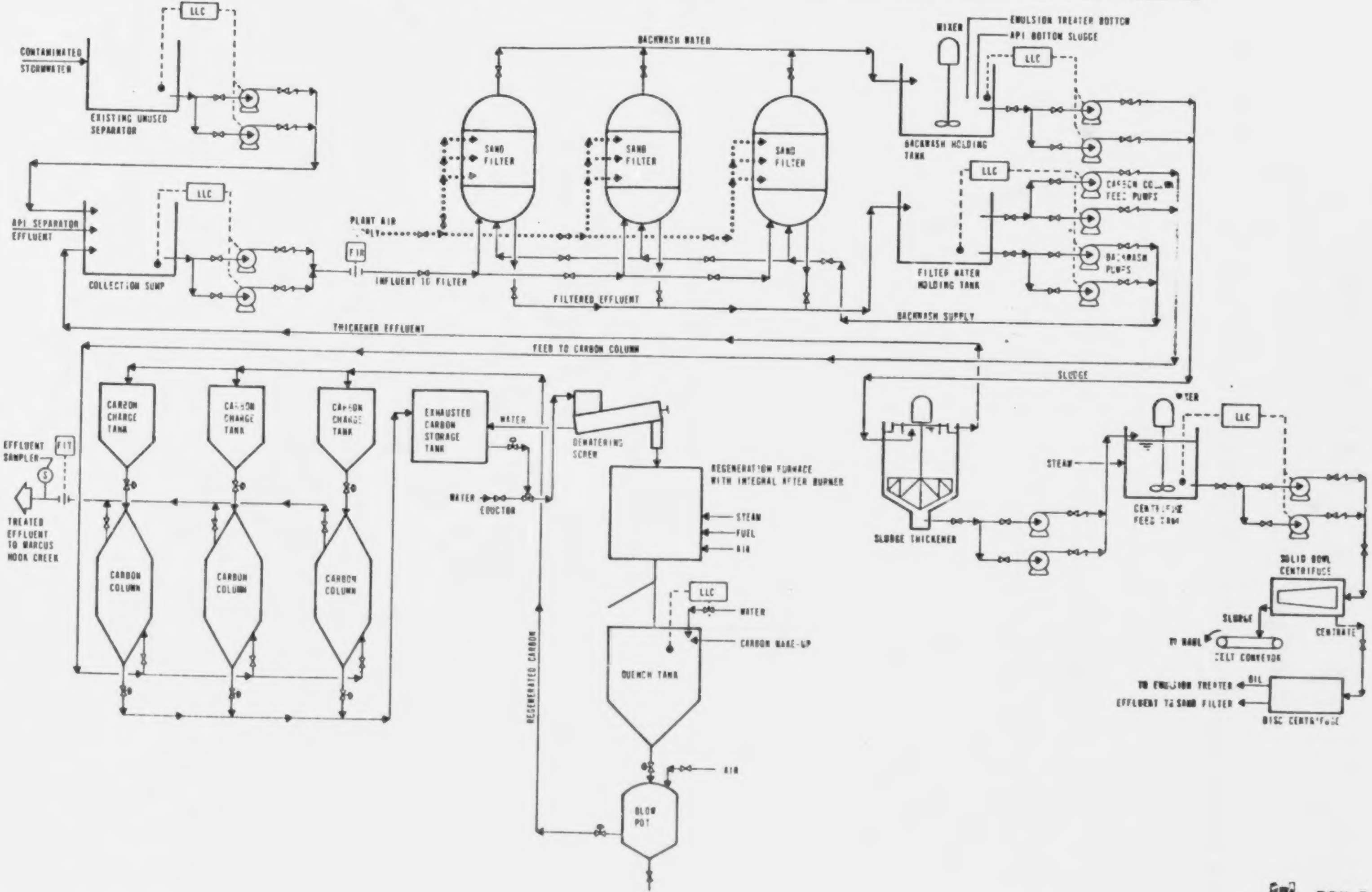
SCHEMATIC FLOW DIAGRAM OF PROPOSED SAND FILTER - ACTIVATED CARBON TREATMENT FACILITIES



CONTAMINATED STORMWATER
LLC
EXISTING UNUSED SEPARATOR
API SEPARATOR EFFLUENT
COLLECTION SUMP
FIR
PLANT AIR SUPPLY
INFLUENT TO FILTER
BACKWASH WATER
SAND FILTER
SAND FILTER
SAND FILTER
FILTERED EFFLUENT
MIXER
EMULSION TREATER BOTTOM
API BOTTOM SLUDGE
BACKWASH HOLDING TANK
CARBON COLUMN FEED PUMPS
FILTER WATER HOLDING TANK
BACKWASH PUMPS
BACKWASH SUPPLY
THICKENER EFFLUENT
FEED TO CARBON COLUMN
SLUDGE
EFFLUENT SAMPLER
FIT
TREATED EFFLUENT TO MARCUS HOOK CREEK
CARBON CHARGE TANK
CARBON CHARGE TANK
CARBON CHARGE TANK
CARBON COLUMN
CARBON COLUMN
CARBON COLUMN
EXHAUSTED CARBON STORAGE TANK
WATER
WATER
EDUCTOR
DEWATERING SCREW
REGENERATION FURNACE WITH INTEGRAL AFTER BURNER
STEAM
FUEL
AIR
REGENERATED CARBON
WATER
CARBON MAKE-UP
QUENCH TANK
AIR
BLOW POT
SLUDGE THICKENER
WATER
STEAM
CENTRIFUGE FEED TANK
SOLID BOWL CENTRIFUGE
SLUDGE
TO HAUL
BELT CONVEYOR
CENTRATE
OIL
TO EMULSION TREATER
EFFLUENT TO SAND FILTER
DISC CENTRIFUGE

Figure IA

TABLE 1

Sand Filtration Pilot Plant Performance

Oil			Suspended Solids			FSUOD		
mg/l		Percent	mg/l		Percent	mg/l		Percent
Inf	Eff	Removal	Inf	Eff	Removal	Inf	Eff	Removal
60	11	79	35	8	77	76	49	35

Activated Carbon Adsorption Pilot Plant Performance

Oil			Suspended Solids			FSUOD		
mg/l		Percent	mg/l		Percent	mg/l		Percent
Inf	Eff	Removal	Inf	Eff	Removal	Inf	Eff	Removal
12.3	1.8	85	8	3	62	57	9	83

TOC			Phenol		
mg/l		Percent	mg/l		Percent
Inf	Eff	Removal	Inf	Eff	Removal
37	13	65	2.7	0.02	99

TABLE 2

Rapid Sand Filter Design Data

Filter Media		
Anthracite		
Depth		2.5 FT
Volume		195 FT^3
Particle Diameter		0.25 FT^3
Sand		
Depth		4.5 FT
Volume		350 FT^3
Particle Diameter		1 mm
Gravel Support		
Depth		1.25 FT
Rated Flow (Each of Three Filters)		1000 GPM
Filter Diameter		10 FT
Center Standpipe		10 IN
Filter Area		78 FT^2
Hydraulic Loading		12.8 GPM/FT^2
Liquid Capacity With Media Installed		4800 GAL
Maximum Allowable Pressure Drop Thru Media		6.5 PSI
Design Pressure		47.5 PSI
Backwash Interval		12 HOURS
Backwash Water Flow	As Percent of Filtrate	1.3%
Low Rate	550 GPM	7.1% GPM/FT^2
High Rate	1960 GPM	25.1 GPM/FT^2
Backwash Air Flow	550 SCFM	7.1 $SCFM/FT^2$

TABLE III

Activated Carbon Adsorption Design Data

Rated Flow (Each of Three Adsorbers)	667 GPM
Adsorber Diameter	10 FT
Adsorber Bed Depth	45 FT
Contact Time (Empty Bed)	40 MIN
Hydraulic Loading	8.5 GPM/FT^2
Design Inlet Pressure	60 PSI
Pressure Drop Thru Carbon	35 LB
Carbon Inventory	
Carbon Bed	92,000 LB
Adsorber Total	100,000 LB
Theoretical Carbon Capacity	0.3 LB TOC/LB Carbon
Carbon Dosage	0.86 LB Carbon/1000 GAL Throughput

Activated Carbon Properties

Filtrasorb 300

Total Surface Area (N_2 BET Method)	950-1050 M^2/g
Bulk Density	26 LB/FT^2
Particle Density Wetted in Water	1.3-1.4 g/cc
Mean Particle Diameter	1.5-1.7 mm
Iodine Number, minimum	950
Ash	Max 8%
Moisture	Max 2%

TABLE IV

Thermal Regeneration Design Data

Furnace	60"x6 Hearth with Integral Afterburner
Regeneration Rate	125 LB/HR
Steam Addition Rate	125 LB/HR
Fuel	Refinery Fuel Gas
Fuel Rate	
Hearth 4	188 CFH
Hearth 6	68 CFH
Afterburner	310 CFH
Combustion Air Rate	
Hearth 4	5000 CFH
Hearth 6	1800 CFH
Afterburner	8120 CFH
Design Temperatures	
Hearth 4	1725°F.
Hearth 6	1750°F.
Afterburner	1250°F.

TABLE V

Wastewater Analyses

Parameter	API Separator Influent	Sand Filter Influent		Carbon Adsorber Influent			Carbon Adsorber Effluent		
	Average	Range	Average	Range	Average	% Reduction	Range	Average	% Reduction
Flow, GPM	1795	1480-1895	1795	735-1585	1450	--	1585	1450	--
Suspended Solids, ppm	165	18-118	75	5-74	25	67	2-67	15	40
Oil, ppm	--	8-144	107	3-66	35	67	1-28	9	40
COD, ppm	--	131-522	341	110-461	239	30	61-199	122	49
Phenol, ppm A	--	0.48-20.9	5.6	0.77-21.8	5.7	--	0.01-0.17	0.05	99
Phenol, ppm B*	--	9.1-20.9	13.5	9.6-21.6	14.0	--	0.43-7.6	4.1	70
BOD$_5$, ppm	590	59-144	95	26-109	68	28	12-92	50	26
FSUOD, ppm	900	75-174	115	35-155	92	20	34-131	67	27

FSUOD Raw Waste Load Reduction = 92.5%

*Following Introduction of Foul Condensate Stripper Bottoms Effluent Concentration Decreasing to Date

TABLE VI

Analyses of Sand Filter Backwash Water

Time After Initiating High Rte (1960 GPM) Backwash Mins.	Suspended Solids ppm
0	87
1	19,370
2	9,010
3	4,160
4	3,010
5	850
6	300

TABLE VII

Analyses of Water Removed from Sand Filters by Pressure Prior to Backwash

Time After Air Pressurization Minutes	Suspended Solids ppm
0	13
1	42
2	296
3	196
4	156
5	77
6	91
7	2,010
8	5,140
9	4,900

TABLE VIII

Wastewater Treatment Plant
Capital Cost

Item	Cost
Engineering	$ 125,000
Surge Basin	30,400
Sand Filters	193,300
Carbon System	358,100
Carbon Charge	120,000
Solids Dewatering	152,300
Tanks	93,200
Pumps	13,100
Building	143,800
Piping	178,400
Electrical	199,400
Instrumentation	133,700
Structural	22,100
Foundations	45,900
Concrete	12,800
Total:	$1,822,400

TABLE IX

Estimated Wastewater Treatment Plant Annual Operating Costs

(Filtration, Adsorption, Regeneration, and Sludge Dewatering)

Labor	$ 44,000
Maintenance	74,000
Power	10,000
Carbon Regeneration ($0.05/LB., Carbon at 3000 LBS/Day)	55,000
Total	$183,000

Includes Steam, Electricity, Labor Fuel and 5% Carbon Make-up.

CASE HISTORY: USE OF POWDERED ACTIVATED CARBON IN AN ACTIVATED SLUDGE SYSTEM

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INTRODUCTION

In an effort to expand the performance of existing biological treatment facilities, full scale trials utilizing powdered activated carbon were conducted at Sun Oil Company's Corpus Christi, Texas Refinery. The main objective of the trials was to reduce the effluent suspended solids loading for compliance with the 1977 NPDES and State permit limitations. Three separate trials were initiated over a one-year period comprising five months of operation with powdered activated carbon addition to the aeration system of the 2.16 MGD biological treatment plant. Although the powdered carbon addition could not guarantee compliance with the 1977 suspended solids' criteria, improvement in the existing system's performance was significant for COD and BOD removal as well as suspended solids. The treatment costs ranged from 1.7 to 4.3¢/10^3 gallons depending on the influent flow and quality. Data have been compiled showing reductions in the refinery's final effluent loadings of up to 56% for suspended solids, 36% for COD and 76% for BOD.

FACILITIES

A simplified flow diagram of the treatment scheme at the Corpus Christi Refinery is shown in Figure 1. The system's operating conditions are outlined on Table 1. The daily average charge to the plant is only half the design capacity; although the peak design rate is often operated during periods of rain and high ballast loading. The refinery wastewater flow (averaging about 600 GPM) is equalized with ballast and contaminated storm water in a 10 MM gallon pond. The combined flow from the pond (averaging about 750 GPM) is pumped through a dissolved air flotation unit for removal of any excess oil and suspended solids. The effluent from the DAF is split between two 760,000 gallon rectangular aeration basins. Air is introduced into each of the basins by two 75 hp floating mechanical aerators. When operating both basins in parallel at average flow conditions, the retention time is about 22 hours; at peak flow, this is reduced to 11 hours. The mixed liquor volatile suspended solids is maintained at about 2200 ppm. With both systems operating, the food to mass ratio averages only about 0.13 lb COD/lb MLVSS or 0.07 lb BOD/lb MLVSS in each basin; this, of course, can be doubled by operating only one aeration system.

Each aeration system is coupled with a 55' diameter x 12' deep clarifier. The overflow from the clarifiers combines for discharge. The settled sludge is collected from each clarifier, combined and returned to the aeration basins. The return rate usually averages about 50% of the charge rate.

OBJECTIVE

Basically, the performance of the biological treatment system is satisfactory and the effluent readily complies with the refinery's NPDES and State permits. With the exception of suspended solids, the limits established for compliance in 1977 are also currently being met. The consistently effective removal of suspended solids in the final clarifier seems to be the only area of concern. Even with substantial organic removal in the biological system, there appear to be two major factors causing the extra suspended solids carryover from the final clarifiers:

- Variability of influent organic and hydraulic loadings. The biological population is thus unstable with erratic growth and variable efficiency.
- Excessive aerator foaming in the aeration basins. This foam, laden with biological solids, tends to carryover into the clarifier and out to the effluent. The problem becomes most severe at high flow periods.

Interim limitations had been set by the State and NPDES permits allowing time to investigate in-plant improvements which could possibly permit compliance with the 1977 TSS criteria without construction of additional facilities. Full scale trials appeared necessary due to the nature of the problems noted -- bench scale studies tended to show excellent settling characteristics which do not reflect the hydraulics of the operating system.

Initial testing was performed with the addition of polymers to the aeration basin effluent. The polymers did improve the solids settling somewhat but their benefit was overshadowed by the problems still being caused by aeration foaming and shock loads. Conversely, defoamers were effective in controlling the foam, nothing more.

In the refinery, every precaution is taken to reduce the possibility of shock loads and spills. However, no matter how efficient, there is no way to completely eliminate the variability: turnarounds, emergency shutdowns and the like. This, coupled with the influx of highly variable loads of ballast, dictated that the treatment plant operation would have to compensate for unstable influent conditions to the plant.

APPLICATION OF POWDERED ACTIVATED CARBON

The addition of powdered activated carbon was initiated in an effort to resolve all the operating problems causing the suspended solids carryover -- the objective being compliance with the 1977 suspended solids' limitations. Although this objective was not achieved, some interesting data resulted. A summary of the three separate carbon trials conducted is shown on Table 2. Unfortunately, it was not possible to operate a "blank" system simultaneously with the carbon system. Therefore, the data obtained 30 days prior to the start of each trial has been utilized as the base period for that trial. As can be noted on Tables 3, 4 and 5, for the most part, the influent loadings of each base period and respective trial are comparable; this is especially true of Trial 3. During each trial, operation was maintined as closely as possible to the conditions observed during the base period. No special problems were encountered that would lead one to believe that any of the trials and base periods' operation were different, especially on the average. Although, the comparison is not ideal, it is relevant, especially in respect to the "real world" effect on the plant's effluent. The percent reductions shown between the base period and each trial are meant as a guide to point up the improvement in effluent quality; the actual values, of course, cannot be taken as absolute. From an operation's standpoint, there appears to be no question that the addition of the powdered activated carbon to the aeration system realizes a significant improvement in the effluent quality and reduces its variability.

The first trial was considerably longer than the last two -- mainly, because the carbon dose was gradually built up in the system over a four-week period; whereas in the other trials, the carbon was batch loaded in a couple of days up to the operating level. The gradual addition of the carbon allowed the daily observation of its effect in order to determine the appropriate loading to be maintained. In order to minimize the amount of carbon needed to load and maintain the system, only one aeration basin was operated during the trials; the same was true of the respective base period. The carbon was manually batch added daily to the dissolved air flotation effluent as it entered the aeration basin. During the first trial it was found that the optimum operating carbon level needed in the aeration system was 450 ppm with approximately 1000 ppm resulting in the recycle sludge. All three trials were conducted at these levels. This requires about 6100 pounds of carbon to charge one aeration system up to operating levels. An easy indication of the carbon level in the system was found to be the foam level in the basin -- the appropriate amount of carbon would eliminate the foam completely; as the carbon level dropped, the foam would build up. Of course, laboratory analysis utilizing a standardized comparison procedure confirmed the operating level of carbon on a concentration basis.

While gradually adding the carbon daily, it was noted that a distinct improvement in the plant performance did not come about until the 450 ppm level was attained -- however, by letting the level drop off gradually, the peak performance could be maintained down to 300 ppm. It was also noted that more frequent additions of smaller quantities appeared more effective than larger batch additions less frequently.

Referring to Table 2, you will note that the carbon addition rate was much higher during the first two trials; this came about for a couple of reasons:

- More frequent batch additions of larger quantities (~1000 pounds at a time) were necessary to compensate for shock loadings. Although the presence of the carbon in the system greatly reduced the chances of a shock that could inhibit the biological activity, it could not guarantee that a reduction in activity would not occur. However, in general, it was found that if caught in time with the addition of a large batch of carbon, a lapse in system efficiency could be effectively brought back up to normal almost immediately without adverse effects on the effluent quality.
- At the time of the third and most recent trial, the biological system was more stable and it took less carbon to obtain the same results. Better methods of equalization had been put into operation and ballast was being successfully treated at a rateable basis.

The flow rate during the third trial averaged 800 GPM versus 625 - 660 GPM for the first two trials (this was due primarily to increased ballast water treatment). The higher flow with the reduced carbon addition rate accounts for the lower 1.7¢10^3 gallon treatment cost compared to Trial 1's 4.3¢. It is important to note that these costs only reflect the carbon usage, the manpower utilized in adding the carbon is not included. More efficient means of carbon addition could, of course, be employed with minimal capital investment but was not deemed necessary for a trial basis.

On Table 6, the treatment costs obtained are summarized along with the reduction in effluent loading observed during each trial.

From this data, one is erroneously led to believe that the efficiency seemed to improve because of a lower carbon dose (and subsequently lower cost). As explained, the higher carbon dosages observed during Trials 1 and 2 are directly attributable to a higher frequency of shock loadings to the system. The only valid conclusions to be drawn from the costs versus efficiency data presented is that the carbon treatment costs range from 1.7¢ to 4.3¢/10^3 gallons depending on the variability of the influent and the frequency of batch additions to solve overload problems. Again, it is important to remember that the percent reductions are determined from the trial versus its pre-trial base case and should only be thought of as a guide for comparison purposes.

Total Suspended Solids Reduction. The average effluent suspended solids data obtained are outlined on Table 3. The reduction in the effluent suspended solids' loading was dramatic, between 49.3% and 55.7%. The existing permit limit is easily met; however, the effluent, at the very low level of 405 lbs/day daily average for Trial 3, still would not comply with the 327 lbs/day limit of the 1977 permit. In addition, although the daily maximum values while using carbon were significantly lower and under better control, several peaks still would occur. Referring to Table 7, in the case of Trial 3, four data points out of 20 were above the 561 lb/day 1977 allowable limit, for 80% compliance; 100% compliance is easily obtainable with the existing permit. Of course, the odds of being able to comply with the 1977 limits are better, but still not acceptable.

Referring to the frequency distributions for Trial 3 plotted on Figures 2 and 3, the reduction in effluent suspended solids with carbon addition becomes very obvious. The chance of complying with the 561 lbs/day 1977 maximum was increased from 40% during the base period to 82% with carbon; of course, these percentages are only relative not absolute. Although the permit is written on a mass basis, the effluent concentration of suspended solids is a basis more easily compared between various facilities and is therefore, shown in Figure 3. On each figure, the flat slope of the carbon trial versus the base period also indicates the more consistent effluent obtainable with carbon treatment, the variability having been significantly reduced.

Organic Removal Efficiency - as mentioned, the addition of powdered carbon also improved the organic removal efficiency of the system. A summary of the influent and effluent COD loadings of the system are shown on Table 4. This table also points up the uniformity of influents between the base period and trial period for Trials 1 and 3. As mentioned, the operation was maintained as consistent as possible for each case. During Trial 2 the influent COD loading was about 25% higher than during the base period -- yet, the effluent loading was 30% lower showing a significant reduction on a relative base. The removal efficiency during Trials 1 and 3 was increased significantly up to 70%

from 62.9% and 54.8% respectively for each trial. The ultimate reduction in COD loading to the effluent being 35.7% for Trial 3 as compared to base period 3.

The daily COD removal efficiencies for Trial 3 are plotted in Figure 4. It can be seen that not only was the removal efficiency significantly increased, the variability of the efficiency was reduced. Again, resulting in an effluent of consistently better quality.

Figure 5 is a frequency distribution plot of the effect of the carbon addition on the effluent COD concentration for Trial 3. Not only does the slope again show more consistent results but, for example, the 95% point has been reduced from 280 ppm down to 150 ppm, a 46% reduction assuming a comparable base.

The effect of powdered carbon on BOD is summarized in Table 5. It is obvious from the influent loadings that the data obtained during Trial 3 are most relevant since the base period and trial had the most comparable influent conditions. Again, as in the case of COD, during Trial 2, the influent loading was 38% higher than the base period; yet, the effluent was 51% lower. The reduction in BOD was most sharply noted during Trial 3 when the effluent BOD never exceeded 6 ppm -- the reduction from the base period was 76%.

The frequency distribution comparing the base period and Trial 3 is shown in Figure 6. Again the results are significant. The curve for the effluent BOD during the carbon addition period is virtually flat, showing definite uniformity and consistency of effluent. Figure 7 denotes the distribution of the percent BOD removals obtained -- again, the curve is relatively flat, the variability being virtually eliminated.

Oil Removal. No data were compiled on oil and grease removal since the system is not required to handle any large amounts of oil. The effluent oil and grease usually averages less than 5 ppm with an occasional peak around 10 ppm; the influent is normally 20-25 ppm. Any improvement would be difficult to observe at these low levels. On occasion, however, the influent oil level can be higher, as did happen during the post period of Trial 2 when there was an upset in the Refinery. The carbon still in the system readily adsorbed the excess oil, keeping it in the sludge. Of course, the sludge had to be removed from the system, thus spending the carbon. However, a possible effluent oil and grease violation was avoided at only the expense of a carbon charge.

SPECIAL NOTE

Sludge wasting had always been erratic and unpredictable in this system due to the variable influent and unstable bug growth. When as stable as possible, about 15,000 gallons per day of recycle sludge would be wasted from one operating aeration system. During the carbon trials the wasting was reduced to 10,000 gallons per day under similar circumstances. The basis for this reduction being that the sludge was considerably thicker so less volume needed to be handled to dispose of the same mass.

SUMMARY

As evidenced by the data presented, the addition of powdered activated carbon to the aeration system of the refinery's existing wastewater treatment facilities did not reduce the effluent suspended solids enough to comply with the 1977 permit limitations. However, significant improvements in the system's performance were observed as follows:

- Improved organic and suspended solids removals and reduced effluent loadings

	% REMOVAL		
Trial 3	Without* Carbon	With Carbon	% Reduction in Effluent Loading
COD	54.8	70.5	35.7
BOd	93.5	98.5	75.8
TSS	-	-	49.3

*Pretrial base period

- More uniform effluent quality
- Clearer effluent
- Elimination of foam in the aeration system
- More consistent sludge wasting at 2/3 the volume
- Reduced chances of biological upsets -- the use of powdered carbon does not eliminate biological upsets but it does appear to reduce the opportunity of their occurance; and when they do occur, it appears to maintain the effluent quality under better control. When caught in time, it was found that a reduction in biological activity can effectively be brought back up to normal by massive batch addition of carbon to the existing operating level.

These improvements were obtained by building up the aeration system to a 450 ppm operating level of carbon with about 1000 ppm in the recycle sludge. The system was maintained at this level by the batch addition of about 100 lbs/day of carbon (or 10 ppm) at an average cost of 1.7¢/10^3 gallons of water treated. The amount of carbon necessary to operate the system for peak performance could be readily determined by observing:

- The aeration basin foam level - the proper operating level of carbon eliminates foam in the system.
- Clarity of the effluent - the presence of carbon in the system removes the tint usually characteristic of biological effluent.

It is important to note that the powdered activated carbon utilized in these trials has a high bulk density of 44 lbs/cu. ft. This becomes an important factor when improved settleability is the primary objective of the carbon addition to the system. In addition, the higher bulk density reduces the opportunity for carbon loss to the effluent.

DISCUSSION

James F. Dehnert: We have done considerable work with powdered carbon on a pilot basis and we have done some of the work that you did. A couple of problems we ran into and I wondered if you had solved them, that is the analysis of the mixed liquor solids. Did you determine actual carbon percentage or was this a calculated value?

Joyce Rizzo: We did it by a standard comparison. What we did was make up standard filters with carbon which we compared. We took samples of our aeration system before we added carbon to it. We added known dosages of carbon and set up a set of standards. So all the numbers we have obtained are 50 ppm, but we could keep track of it pretty easily.

James F. Dehnert: We had not devised a system to determine how much carbon was actually in our system at any one time. The second question: you said you didn't test very many parameters. We have a problem in California with meeting fish toxicity, did you ever run any tests on that?

Joyce Rizzo: Everyone knows that refinery effluent is not toxic. Maybe California is different – they may have a higher breed of fish down there, I don't know. Obviously, we didn't evaluate toxicity.

Les Lash: You mentioned holding about 450 milligrams per liter of activated carbon, Joyce, in your aeration basin, I guess. What is the retention time in that aeration basin?

Joyce Rizzo: About 12 hours at average operating conditions.

Les Lash: When we ran the pilot plant on municipal waste for the EPA on powdered activated carbon in Salt Lake, we used reactive clarifiers and if you didn't allow enough settling, of course the effluent went over black. Now that is a little different than the clear you were talking about.

Joyce Rizzo: The only time we ever had a carryover problem with carbon was during a time when the bug population was upset and they would tend to take the carbon with them. If they were going out, they weren't going to leave the carbon behind. On a normal basis we had no problem with carbon carryover at all. It stayed right with the sludge. In fact, it improved the settleability tremendously. If you look at the clarifier, it has the appearance of being black; of course, the aeration system would turn black versus the dark rich brown color and it appeared like it was all carbon. The carbon color would take over completely, and if you looked at the clarifier surface, it appeared black but the effluent water was virtually clear.

Milton Beychok: I am just a bit curious, I don't know if there is anyone here from duPont or not, but something like four years ago, duPont first used this and called it PACT, powdered activated carbon treatment, and they were licensing it. Does the use of this involve any patent problems or royalty on the part of duPont?

Joyce Rizzo: No, this is quite a different system than what duPont is utilizing in their PACT project, they are also utilizing a regeneration system which I believe is also a part of their patent on that. We used ICI carbon, and the system that we used was outlined to us from ICI as to how to operate. I don't think we did anything really different. I have talked to many people who are also using powdered carbon in their aeration system in a similar manner.

Ed Sebesta: I note you have a centrifuge for your waste activated sludge there. Did you continue to use a centrifuge both before and after carbon addition and what was the effect?

Joyce Rizzo: We don't use a centrifuge all the time by the way, only when we have to. We have plenty of land out there for land farming and a lot of times put the sludge out wet from the aerobic digester. We did not see any real difference in our sludge handling characteristics on the solid waste handling system - none at all. Actually, the amount of carbon that we used - our aerobic digester is three-quarter million gallons like our aeration system - and the amount of carbon that we used and the amount that was wasted was virtually lost in the system.

Ed Sebesta: I have another question and you indicated that the effluent was very clear. I think the data indicated about an average of 40 parts per million suspended solids. This is pretty high for a very clear effluent, do you have any explanation for the concentration numbers?

Joyce Rizzo: Very fine solids. Color really is what I am talking about. 40 ppm does not represent optimal operation, 10-20 ppm would be more representative of the best effluent obtainable with the carbon. The solids that would settle out by the way would be ones that would settle out after hours. You could take a sample of the effluent and you wouldn't think there were suspended solids in it, but if you let it sit for a while, the solids that would settle would be very, very fine. I would say about half the solids that went out in the effluent were carbon solids. Very, very fine solids.

Pat DeJohn: I'd like to make a couple of comments. One that Mr. Lash made, the carbon that you were using has a density of about 45 pounds per cubic foot, and consequently it settles very rapidly. I believe what they were using out at Salt Lake was a carbon that had a density of about 15 pounds per cubic foot. The higher density is the reason the carbon doesn't go out over the weir. The other thing about the patent situation, duPont just got a patent issued about two months ago on the PACT process and right now there are some negotiations going on with respect to that.

Janis Butler: You mentioned sometime just spreading the wet waste activated sludge. Do you experience any odor problems?

Joyce Rizzo: No - none at all. If we put it out wet, the solids settle rapidly, and there is no odor problem at all. We are using (I have been gone now from Corpus Christi for about six months), but at the time I left we were using the centrifuge all the time for the waste.

Anonymous: Do you add carbon continuously?

Joyce Rizzo: Corpus Christi has just purchased another load of carbon for usage. As I understand it, their main goal is to use it mostly for batch addition for shock loadings and things like that.

Fred Goudy: Does the use of powdered carbon have any long range implications with regard to the operation of the activated sludge plant at Corpus Christi?

Joyce Rizzo: They are using it.

Fred Gouay: Continuously?

Joyce Rizzo: I am not sure, I can't answer that for fact right now. I know they have just purchased some more carbon, and I know they have it in stock and I know that their intentions are to use it. Now whether they will use it all the time, I don't know at this time. I might mention what I think about carbon application in the aeration system. Like I said, although we really were oriented to suspended solids removal, it is obvious that some of the other things that I have mentioned about the system are very true. That is, if you have a plant that is sitting there hydraulically loaded and you need more capacity, it seems to help and gives you that extra capacity that you need. As I mentioned none of the reductions that I presented, of course, should be taken as absolute numbers because it was pretrial versus trial period. But there is no question that the improvement in the plant performance is there and I think the improvement is really dependent on the variability of your influent.

Dave Story: You mentioned adding polymers; could you elaborate a little bit more on that?

Joyce Rizzo: Yes, we didn't do too much work with polymers because it was the very first thing we tried to reduce suspended solids. We were adding about 5 or 6 parts per million of some polyelectrolytes to our aeration basin overflow and we saw a reduction in effluent suspended solids and a little bit better settling characteristics, but nothing very significant. I think this is mostly due to our foaming problem because we still had a lot of foam carrying over to the clarifier which is a significant problem.

Anonymous: How do you account for the reduction in sludge wasting?

Joyce Rizzo: We didn't have to maintain as many bugs in the system and they didn't have to work as hard. But the real reduction was in volume not mass. The recycle sludge was thicker and more uniform with carbon addition.

BIOGRAPHY

Joyce A. Rizzo is a staff engineer in the Advanced Management and Methods Department of Suntech, Inc., a subsidiary of Sun Oil Company. She is based in Marcus Hook, Pennsylvania. Ms. Rizzo joined Sun Oil in 1971 as a process engineer at their Marcus Hook Refinery. Prior to her move into Suntech six months ago, she spent three years in Process Engineering at Sun's Corpus Christi Refinery. She holds a B.S. in Chemical Engineering from Northeastern University in Boston.

TABLE 1

"OPERATING CONDITIONS OF WASTEWATER TREATMENT PLANT"

FLOW		
Daily average	1.08 MGD	
Daily maximum	2.16 MGD	
Design	2.16 MGD	
BIOLOGICAL SYSTEM	2 - 760,000 Gal. Rectangular Aeration Basins 2 - 75 HP. Floating Aerators/Basin	
Recycle	50% of Charge Rate	
MLSS	3000 PPM	
MLVSS	2200 PPM	
Retention (Per Basin)	11 Hours at Maximum Design Rate 22 Hours at Average Operating Rate	
Sludge Age	12 Days	
SETTLING	2 - 55 Ft. Diameter Circular Clarifiers	12 Ft. Deep
	Average Rise Rate, GPD/FT^2	227
	Peak Rise Rate, GPD/Ft^2	455

SOLIDS HANDLING

1 - 760,000 Gallon Aerobic Digester
1 - Solid Bowl Centrifuge
4 Acres of Land Farm

Wasting Rate	30,000 GPD
VSS	7,500 PPM

TABLE 2

"SUMMARY OF POWDERED ACTIVATED CARBON ADDITION TRIALS"

Aeration System: 450 PPM PAC
Recycle System: 1000 PPM PAC

				Average Carbon Dosage			Treatment Cost*
		Period	Duration	Lbs/D	Lbs/10^3 Gal	PPM	¢/10^3 Gal
Trial	1	Sept.-Nov., 1974	82 Days	179	0.20	24	4.3
Base Case	1	August, 1974	30 Days	-	-	-	-
Trial	2	May, 1975	28 Days	152	0.16	19	3.5
Base Case	2	April, 1975	30 Days	-	-	-	-
Trial	3	August, 1975	26 Days	87	0.076	9	1.7
Base Case	3	July, 1975	31 Days	-	-	-	-

*At 22 ¢/Lb

TABLE 3

"EFFECT OF POWDERED CARBON ON DAILY AVERAGE EFFLUENT SUSPENDED SOLIDS"

1977 Permit: 327 Lbs/Day Daily Average

	Flow	Permit	Effluent		%
	GPM	PPM	PPM	Lbs/Day	Reduction
Base Case 1	626	43	115	861	
Trial 1	629	43	50	381	55.7
Base Case 2	645	42	163	1262	
Trial 2	657	41	72	565	55.2
Base Case 3	839	32	79	799	
Trial 3	799	34	42	405	49.3

TABLE 4

"EFFECT OF POWDERED CARBON ON COD"

	Flow	Influent		Effluent		%	%
	GPM	PPM	Lbs/D	PPM	Lbs/D	Removal	Reduction
Base Case 1	626	459	3445	170	1277	62.9	
Trial 1	629	457	3446	135	1020	70.4	20.1
Base Case 2	645	343	2658	266	2059	22.5	
Trial 2	657	444	3500	183	1445	58.7	29.8
Base Case 3	839	367	3698	166	1670	54.8	
Trial 3	799	379	3632	112	1073	70.5	35.7

TABLE 5

"EFFECT OF POWDERED ACTIVATED CARBON ON BOD"

	Flow	Influent		Effluent		Removal	Reduction
	GPM	PPM	Lbs/D	PPM	Lbs/D	%	%
Base 1	626	152	1144	15	116	89.9	
Trial 1	629	213	1607	15	114	92.9	1.7
Base 2	645	152	1173	30	232	80.2	
Trial 2	657	227	1898	13.5	113	94.0	51.3
Base 3	839	188	1895	12	124	93.5	
Trial 3	799	207	1981	3	30	98.5	75.8

TABLE 6

"COMPARISON OF CARBON TREATMENT COSTS AND SYSTEM PERFORMANCE"

	Dose			% Reduction* In Effluent Loading	
	PPM	¢/10^3 Gal.	TSS	COD	BOD
Trial 1	24	4.3	55.7	20.1	1.7
Trial 2	19	3.5	55.2	29.8	51.3
Trial 3	9	1.7	49.3	35.7	75.8

*As Compared to Respective Base Case

TABLE 7

"EFFECT OF POWDERED CARBON ON DAILY MAXIMUM EFFLUENT SUSPENDED SOLIDS"

1977 Permit: 561 Lbs/Day Daily Maximum

	Peak Maximum Lbs/Day	Data Points	Number of Times 1977 Maximum Was Exceeded
Base Case 1	1835	22	17
Trial 1	1432	57	12
Base Case 2	2124	22	19
Trial 2	1889	20	7
Base Case 3	2688	22	14
Trial 3	971	20	4

FIGURE I

TREATMENT PLANT FLOW DIAGRAM

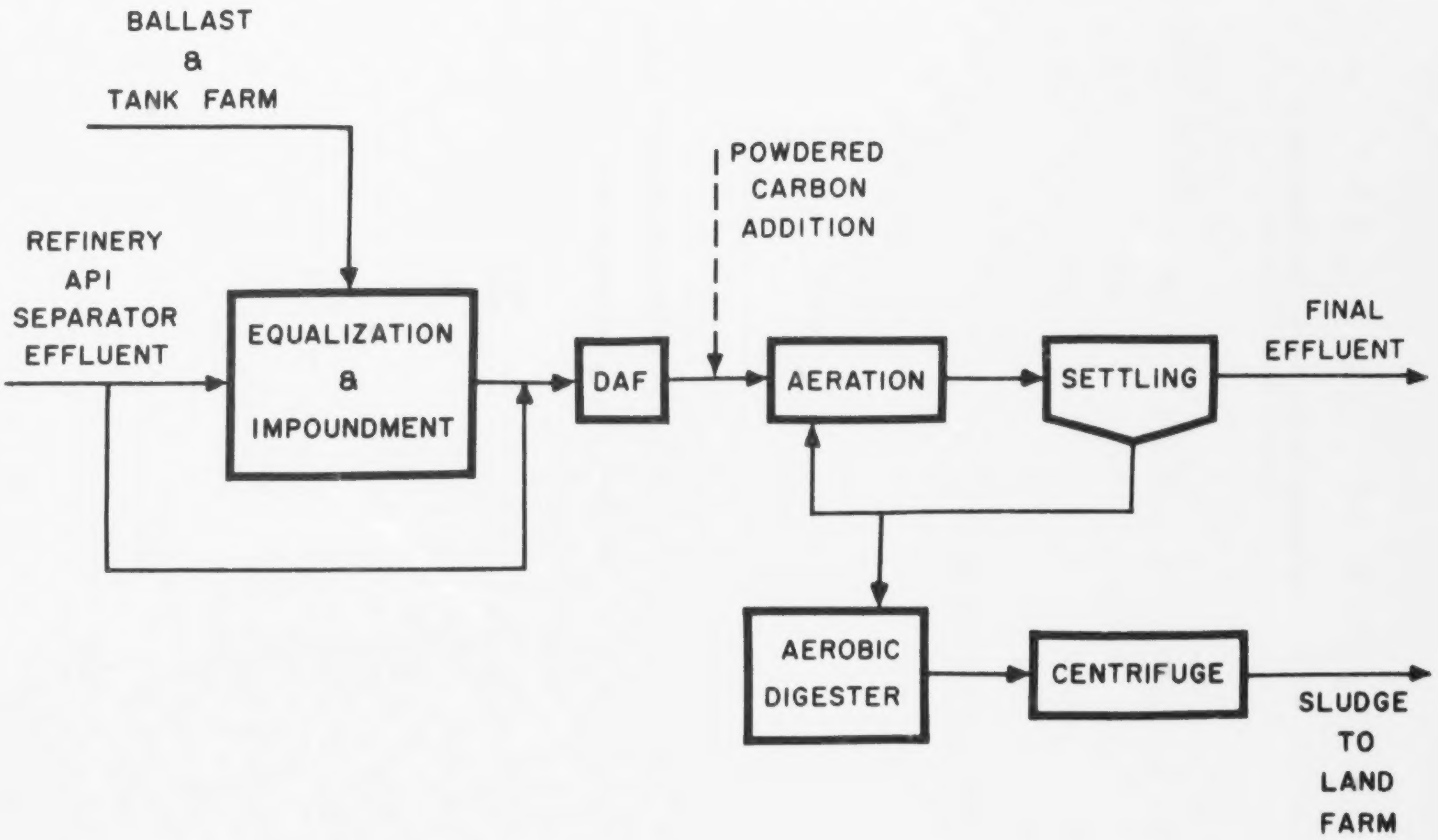

BALLAST & TANK FARM
REFINERY API SEPARATOR EFFLUENT
EQUALIZATION & IMPOUNDMENT
DAF
POWDERED CARBON ADDITION
AERATION
SETTLING
FINAL EFFLUENT
AEROBIC DIGESTER
CENTRIFUGE
SLUDGE TO LAND FARM

FIGURE 2

EFFECT OF POWDERED CARBON ON EFFLUENT TSS LOADING

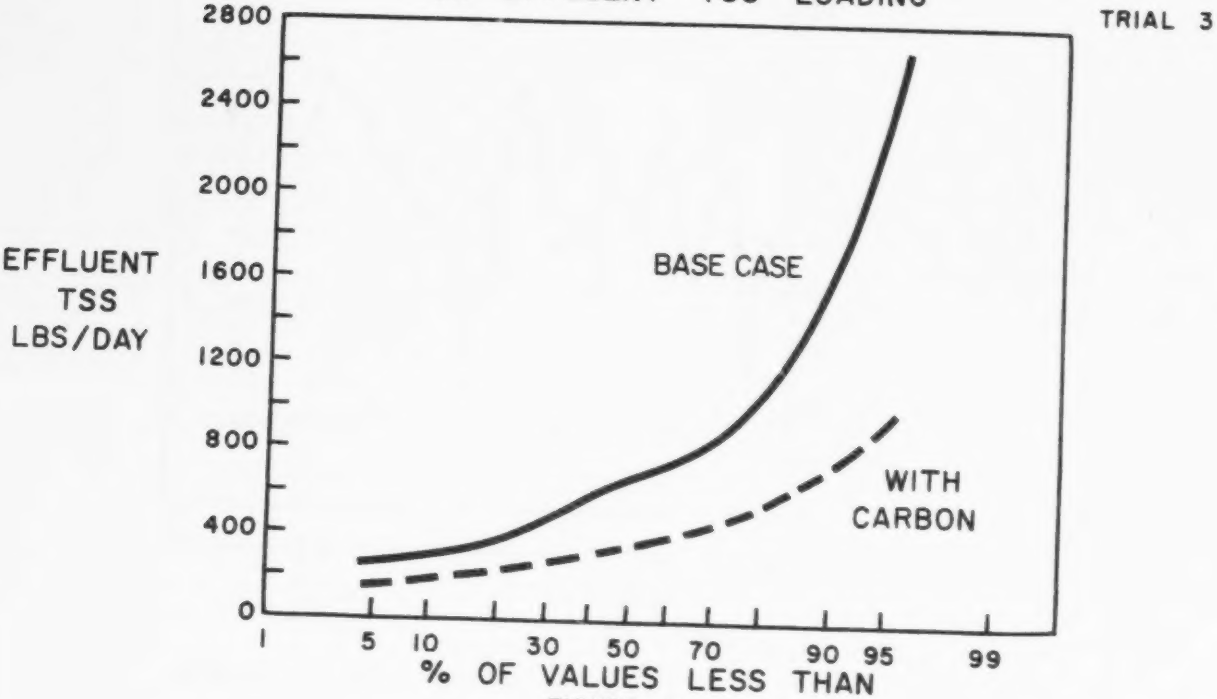


FIGURE 3

EFFECT OF POWDERED CARBON ON EFFLUENT TSS

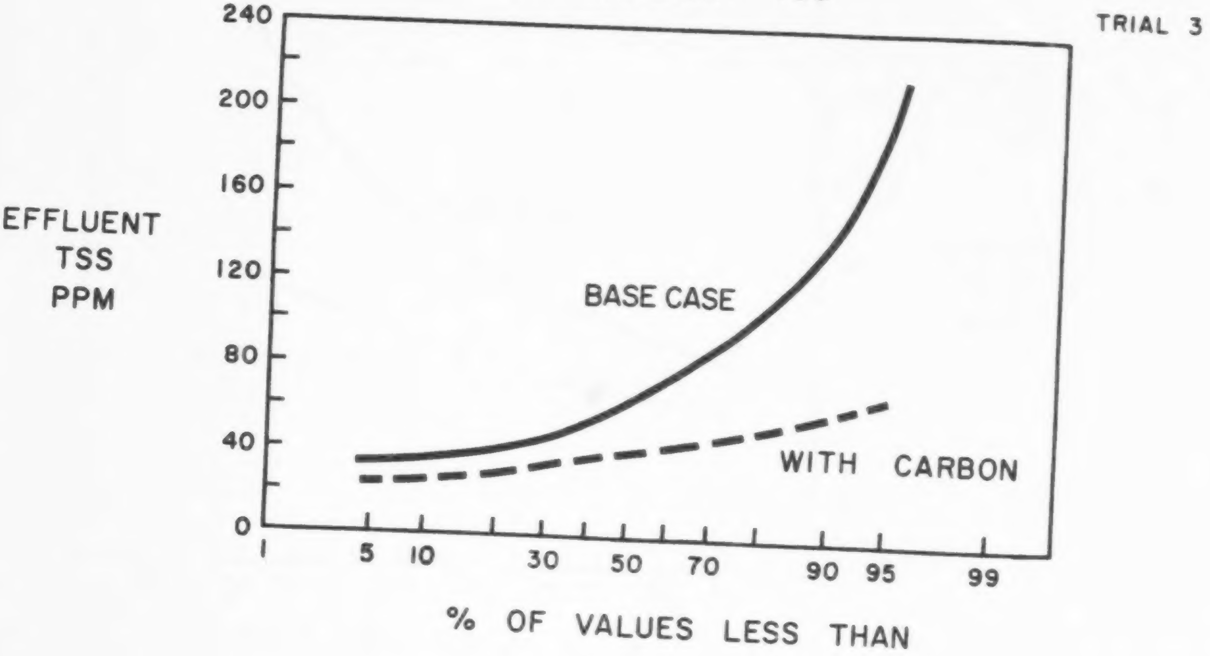


FIGURE 4

COMPARISON OF COD REMOVAL EFFICIENCY

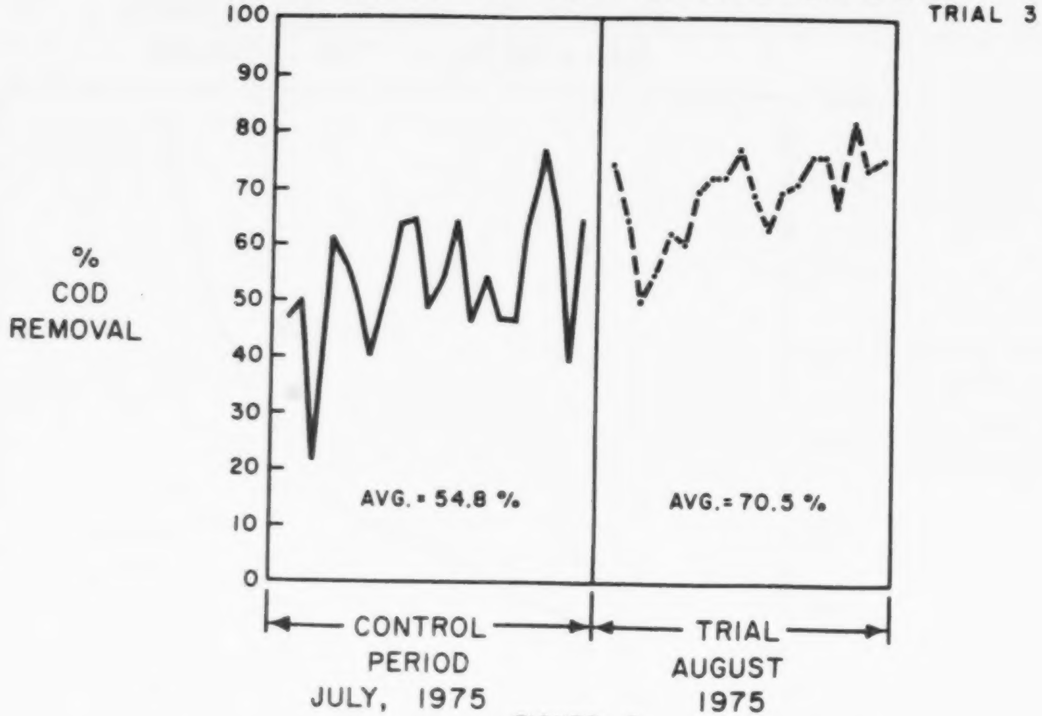


FIGURE 5

EFFECT OF POWDERED CARBON ON EFFLUENT COD

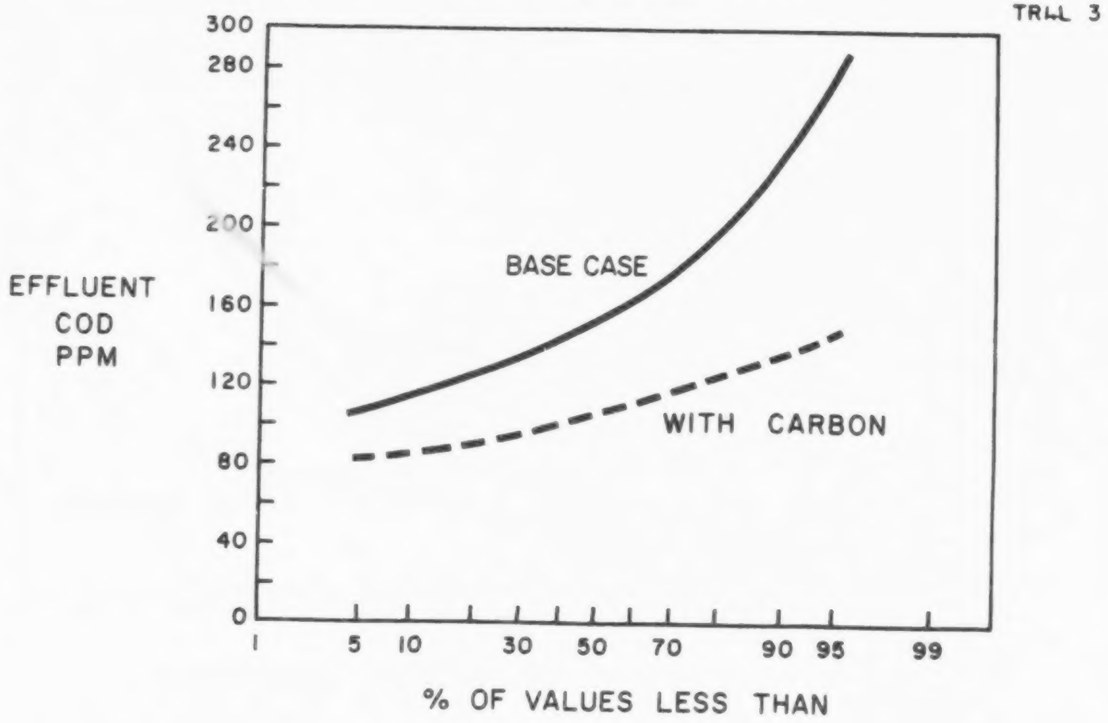


FIGURE 6

EFFECT OF POWDERED CARBON ON EFFLUENT BOD

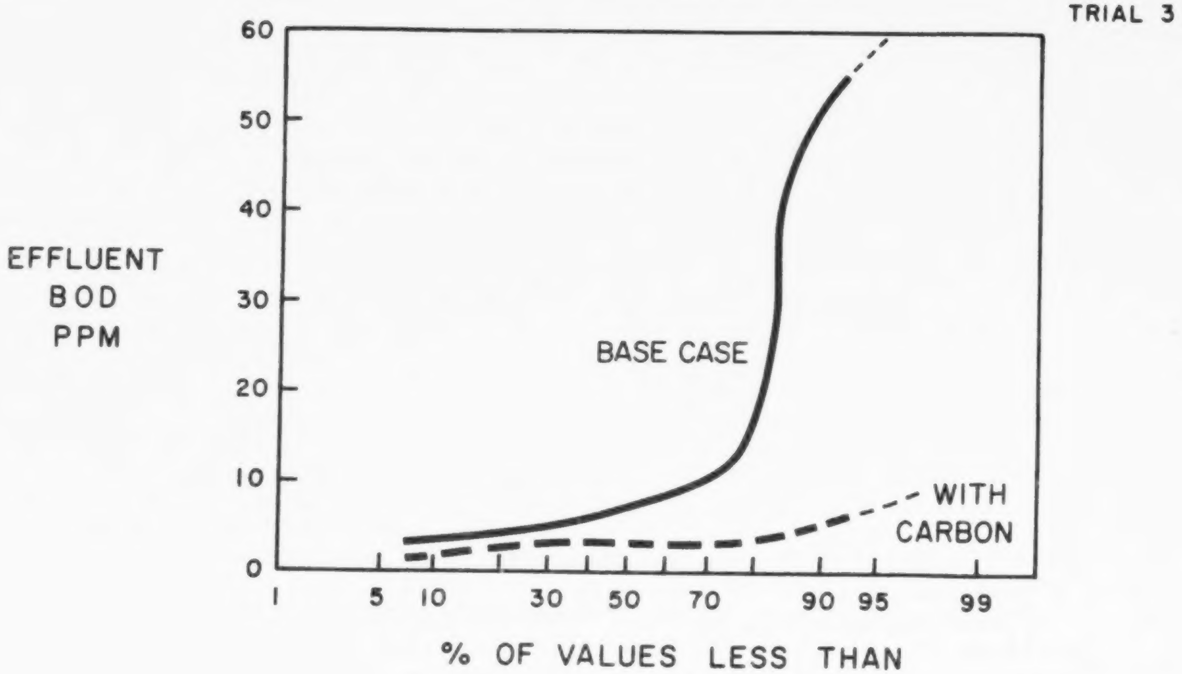
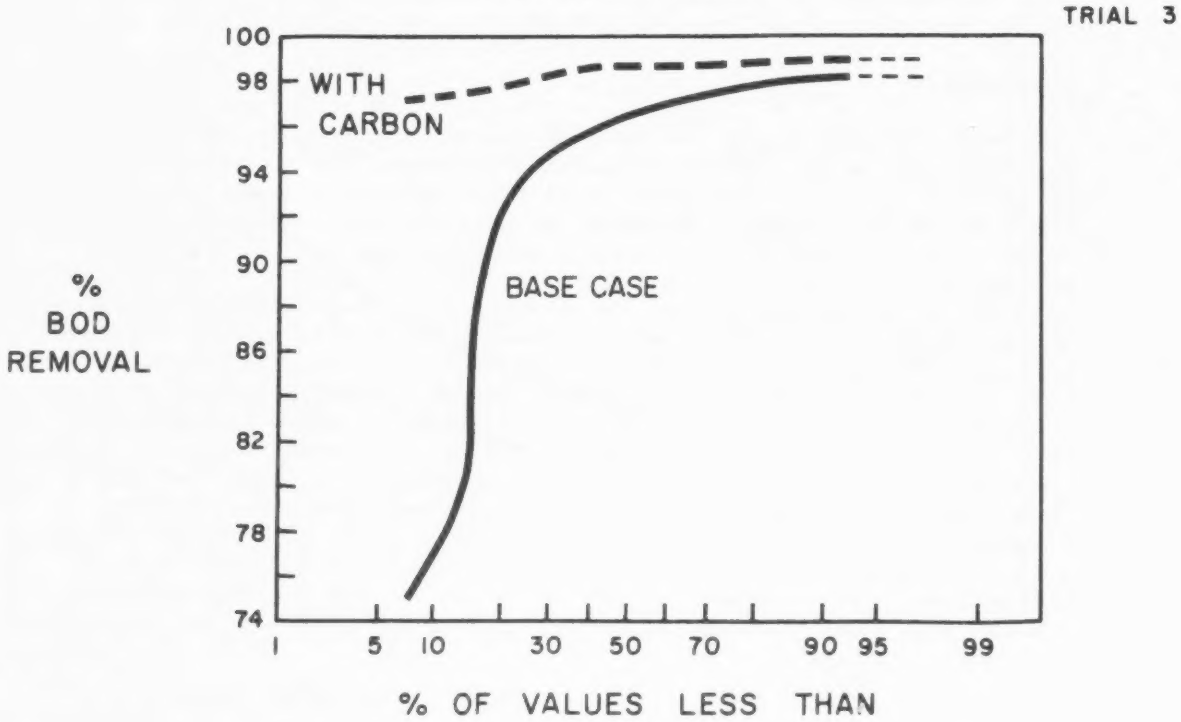


FIGURE 7

EFFECT OF POWDERED CARBON ON BOD REMOVAL



CASE HISTORY
THE USE OF POWDERED ACTIVATED CARBON WITH A BIODISC-FILTRATION PROCESS FOR TREATMENT OF REFINERY WASTES

J.F. Dehnert
Environmental Director, Avon Refinery, Lion Oil Co.

ABSTRACT

A description of the development of a supplemental petroleum waste water treating plant utilizing a Rotating Biological Surface Unit and Powdered Activated Carbon followed by clarification and filtration from laboratory and pilot plant studies through construction, start up and operation to meet July 1977 NPDES discharge requirements.

Starting in 1972 Pilot Plant studies were conducted to compare the performance of activated sludge, trickling filter, RBS and activated carbon absorption processes in treating the Avon Refinery Waste Water. The primary objection was to meet the EPA guideline discharge limits plus the California State limits on fish toxicity. After several months of study the treatment scheme of a RBS Unit plus solids removal facilities was selected to meet the Federal standards and powdered activated carbon was selected to meet the toxicity limits.

INTRODUCTION

With the adoption of the 1972 Amendments to the Clean Water Act, the Staff at the Avon Refinery near San Francisco, then operated by Phillips Petroleum Co. embarked on an investigative program to determine the waste water treatment necessary to meet the limitations which would eventually be placed on the refinery discharge through the NPDES Program. At that time and until January 1975, the refinery discharge was already subject to limitations imposed by the California Regional Water Quality Control Board on 5-day BOD, oil and grease, settleable solids, suspended solids, coliform and fish toxicity. In addition, limitations were in effect on receiving water quality with respect to pH, dissolved oxygen, undissociated NH_4OH, chromium, lead, H_2S, Fish Toxicity, floating oil, discoloration or turbidity and odor. The existing waste water treatment included sour water stripping, API gravity separation, dissolved air flotation and pH equalizing surge ponds followed by a 108-acre bio-oxidation pond. The company had also segregated the refinery sewers so that as much as possible of uncontaminated storm run off could bypass the process water treatment. This storm run off was combined with the bio-oxidation pond effluent and discharged in an underwater diffuser in the main channel of an arm of San Francisco Bay which receives the Central California Valley drainage. This treating process is illustrated in Figure 1.

INVESTIGATION

At the start of the investigation, no specific Federal limitations had been determined and, therefore, the studies were mainly concerned with a comparison of generally accepted methods of waste water treatment to determine which of these would be most effective in removing or reducing the known pollutants in the Refinery effluent. A primary objective was to determine a treatment scheme that would result in a waste water discharge that would meet the more restrictive California State fish toxicity limitations that were being proposed.

In early 1972, working with an engineering contractor, three pilot plants were installed at the Refinery with a slip stream of the waste water going to the bio-oxidation pond serving as the raw feed. These units were an air agitated activated sludge unit, a 21-foot trickle filter and a four-column granular activated carbon unit preceded by a mixed media filter. These plants were operated from June 1972 through 1973 in parallel or in series under wide variations of operating conditions such as hydraulic loading, recycle rates and suspended solids concentrations.

During this period of operation, different sets of tentative EPA guidelines were issued for the Petroleum Industry. In each case, the effluent from the biological treating pilot plants failed to meet these guidelines and the proposed California fish toxicity standards. From the experimental data it appeared the only way these limitations could be met was by the use of activated carbon at high regeneration rates as a final treating step. It appeared that the waste water contained some non-biodegradable or at least "refractory" organic material as indicated by COD and TOC tests.

In the Spring of 1973, information was received describing the rotating biological surface units which were being proposed for treating industrial waste as an improved alternate to the other biological treatment systems. There were several advantages claimed for this process such as high biomass concentration; low volume, high density sludge production and low power requirement.

Subsequently, arrangements were made to install a four stage pilot rotating biological surface unit at the refinery and to compare its performance with the other pilot plants.

The RBS test program consisted basically of three periods determined partly by a difference in the quality of raw waste water and partly by the type of operation of the unit. During the first period, a direct comparison was made between the trickle filter, the activated sludge and the RBS units with the same feed going to all three units. For the second test period, the feed rate to the RBS unit was reduced to a very low figure to establish nitrifying bacteria in the bio-mass. During the third period, a series of hydraulic loading tests were performed where the rate was varied from 1/2 gpm to 18 gpm representing hydraulic loading of 0.2 to 6.8 gal/day/sq.ft. of surface area.

As a result of the pilot plant study, it was concluded that the removal of organic pollutants by the RBS unit compared favorably with the trickling filter and the activated sludge processes and, for some waste water parameters, the RBS unit appeared to be superior. The pilot plant operation verified most of the claims made by the manufacturer, particularly with respect to energy requirements and ease of operation.

The removal of organics by the RBS unit was very similar to the trickle filter and the activated sludge with each unit able to achieve about the same percentage removal and final concentrations in the final effluent at their optimum operation.

A portion of the test program was devoted to establishing nitrification and determining the relationship between hydraulic loading and the degree of conversion of ammonia to nitrate. This was accomplished by operating the unit at a very low feed rate and adding sodium bicarbonate to increase the alkalinity. At the low rate, it was possible to lower the ammonia concentration from 15 to 20 mg/1 to less than 1 mg/1; however, as the feed rate was increased, nitrification decreased and eventually stopped altogether. Contrary to what was expected, over 50% of the conversion of ammonia to nitrate took place in the first stage. From the data obtained, it was concluded that, if nitrification is desired in a commerical unit, it would have to be designed for about one-half the hydraulic loading that would be required for organics removal.

One of the most noticeable differences between the RBS effluent and the effluent from the other bio systems was the suspended solids content. Although the suspended solids did increase with feed rate, even at relatively high hydraulic loading, the RBS effluent had lower suspended solids than the best operation of the other processes. At low feed rates, the RBS effluent after 30 minutes of settling, exhibited a sparkling appearance that was achieved on the other processes only by filtration or activated carbon treatment of the effluent.

Static bioassays were conducted weekly on samples of the various pilot plant effluents using the APHA standard methods to determine the 96-hr. median toxicity (TLm). Although the RBS unit was not the answer to the toxicity problem at the Avon Refinery, in general, this effluent was less toxic than the effluents from either the trickling filter or the activated sludge. Activated carbon absorption remained as the only waste water treatment that would produce a completely non-toxic water (100% survival) from the waste water stream.

Activated carbon treatment data are presented in Tables I through VIII.

Table I presents early data showing the effect on fish toxicity of treating various RBS effluents with powdered activated carbon.

Tables II and III present data on the effect of powdered carbon on other parameters and indicate that toxicity is improved although other parameters are not greatly affected.

Tables IV and V illustrate the effect of pH changes on toxicity and possibly the ability of carbon to absorb the toxicants.

Tables of VI and VII show comparisons of two different powdered activated carbons and indicate that selection of the proper carbon source can make a very great difference in the ultimate success of carbon treatment.

Table VIII is a part of a very large table of data obtained on a granular carbon test conducted over a six month period. It is presented to further illustrate that long after the carbon was "exhausted" with respect to COD removal it would continue to produce a non toxic effluent and that it could be rejuvenated by a hot water backwash.

By the time these pilot plant studies were complete, the final guidelines had been issued by EPA and the N.P.D.E.S. permit for the refinery had been issued by the Regional Water Quality Control Board. This permit outlined not only the discharge limits but a compliance schedule for submitting a conceptual plan, completion of Engineering, start of construction and completion of construction. At this time a thorough review was made of all the accumulated pilot plant data and the conceptual plan developed. It appeared that of the many parameters of water quality, COD, suspended solids and fish toxicity would control the design of the treatment system. Included in the consideration was the volume of water which varied considerably with the seasonal storm water entering the process or oily sewers, since practically all of the annual rainfall in this location occurs between the first of November and the first of April. Several alternate plans were considered but all were basically a supplemental biotreatment, solids removal and activated carbon treatment.

During the long period of monitoring the raw waste quality it became evident that treating requirements were also cyclic in that both COD and toxicity increased during the winter months but during part of the year the discharge would probably meet the 1977 limits without much, if any, additional treatment. In our studies with granular activated carbon we noted that in several instances long after the carbon was "exhausted" with respect to removal of COD it would still produce a non toxic water. From this information it appeared the biotreating system should be capable of handling wide variation in waste loading and that a carbon system should be designed to be used only when necessary. From Capital cost considerations, possible ease of handling and the indication that relatively small quantities would be required, the decision was made to use powdered carbon on a periodic and throw away basis rather than use a granular bed system.

In the summer of 1975 the conceptual plan illustrated in Exhibit II was put out for bids to Engineering-Construction Firms as a "turn key" project. As a result Engineering was completed by December 1975, field construction started in February 1976, and completed by January 1, 1977, all well within the compliance schedule.

At this writing the treating facilities are still in the process of starting up primarily because of an extraordinary length of time required for biomass to develop on the RBS units and then delays in correcting minor difficulties with certain mechanical equipment, instruments and electrical control systems.

Our principle concern was the difficulty in establishing the biomass. During the pilot plant phase we had started up three different pilot plants charging similar waste water and in all cases a good growth was established within 3 to 4 weeks. However, in the case of our commerical unit after four weeks there was only a very slight indication of biogrowth on the first stage. It was determined that low water temperature and relatively low soluble BOD were responsible for the apparent lack of bioactivity.

With increased temperature and the addition of higher strength waste water, supplied with a portable pump for 10 days, we observed an increase in the growth of the biomass extending through all three stages. Up to this point only the RBS and the clarifiers were in operation with the plant effluent returning to the feed surge ponds. However, with the establishment of biomass, the filter, polymer injection system and sludge digester were all put into operation. The carbon system was operated for a short period primarily to test it mechanically.

Only limited data has been obtained at this time however, they indicate the plant will perform satisfactorily and the waste water discharge will be in compliance with the July 1, 1977 limitation.

BIOGRAPHY James F. Dehnert

James F. Dehnert is the Environmental Director for the Avon Refinery of Lion Oil Company at Martinez, California. He has a B.S. degree in Chemical Engineering and a B.S. degree in Chemistry from Washington State University. He has been employed at this Refinery for thirty years with various assignments in Techanical Service, Economic Planning and Unit Operations. He served as an Area Operation Supervisor before becoming involved in Environmental assignments.

EXHIBIT I

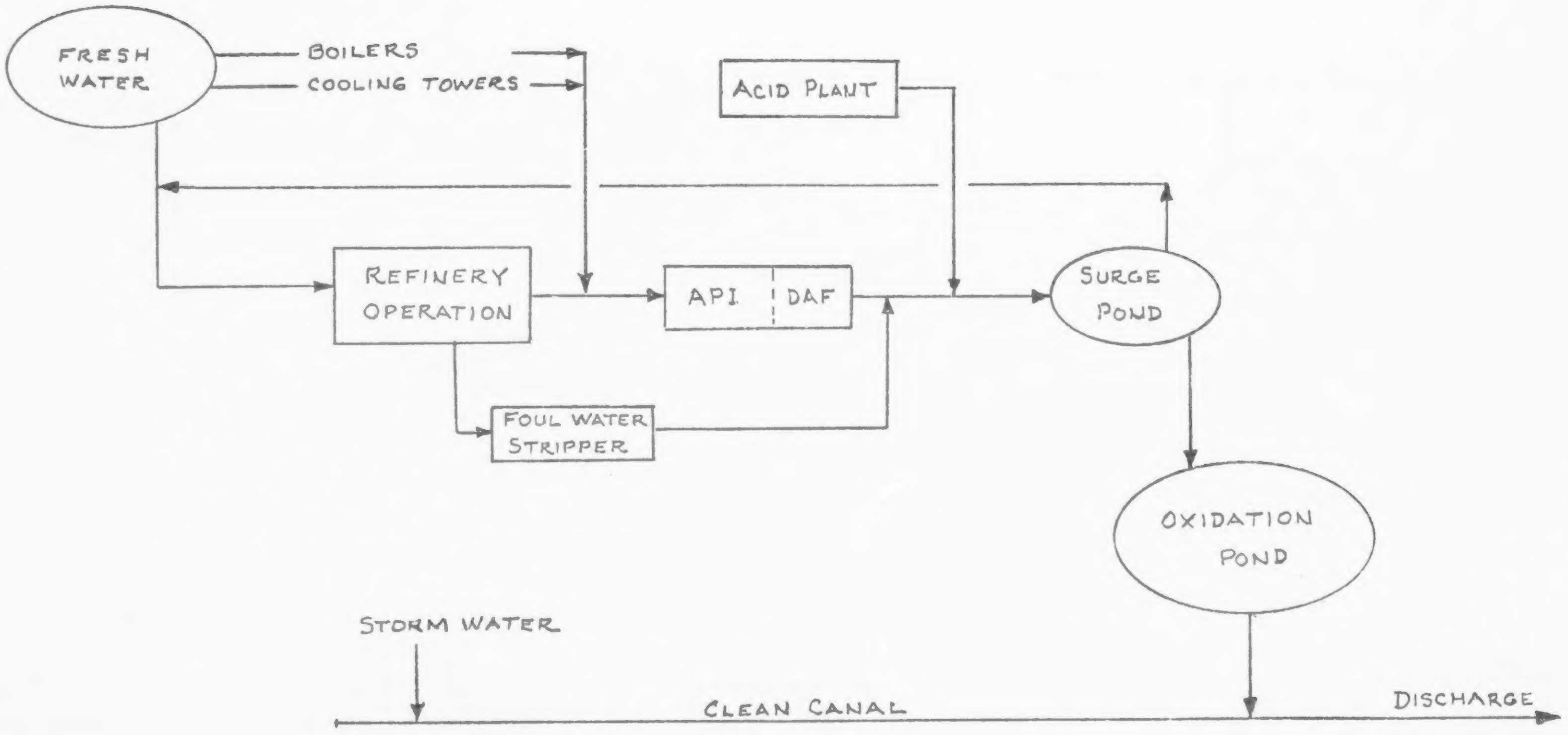

FRESH WATER
BOILERS
COOLING TOWERS
ACID PLANT
REFINERY OPERATION
API
DAF
SURGE POND
FOUL WATER STRIPPER
OXIDATION POND
STORM WATER
CLEAN CANAL
DISCHARGE

EXHIBIT II

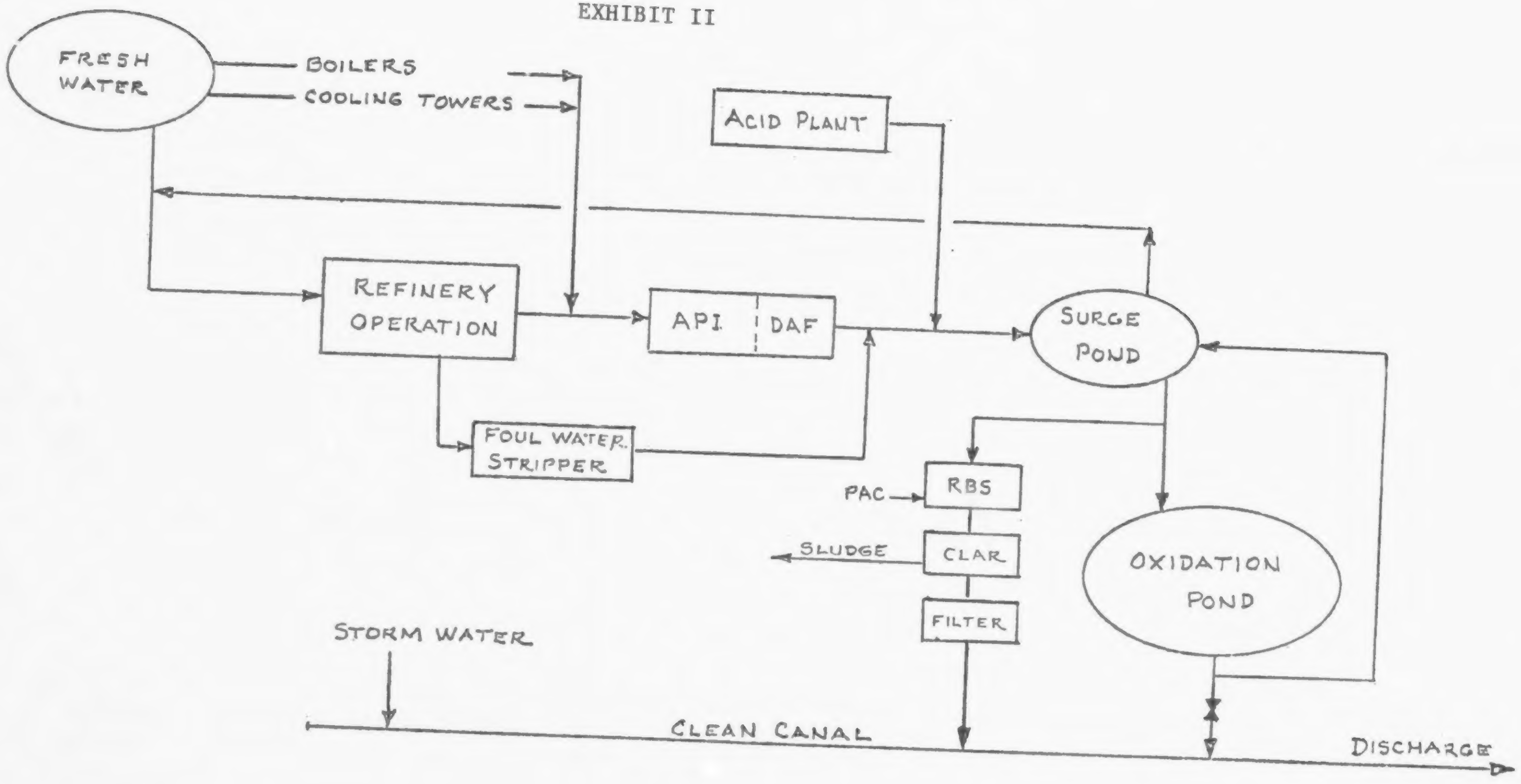

FRESH WATER
BOILERS
COOLING TOWERS
ACID PLANT
REFINERY OPERATION
API
DAF
SURGE POND
FOUL WATER STRIPPER
PAC
RBS
SLUDGE
CLAR
FILTER
OXIDATION POND
STORM WATER
CLEAN CANAL
DISCHARGE

TABLE 1

TREATMENT OF RBS EFFLUENT WITH POWDERED ACTIVATED CARBON

Test	Sample	TLm	or	Survival*
No. 1	RBS Feed	74		
	RBS Eff	90		
	RBS Eff + 20 ppm PAC			90%
No. 2	RBS Feed	80		
	RBS Eff			90%
	RBS Eff + 10 ppm PAC			100%
No. 3	RBS Feed	80		
	2nd Stage RBS	92		
	2nd Stage RBS + 10 ppm PAC			90%
No. 4	RBS Feed	< 35		
	RBS Eff	< 75		
	RBS Eff + 10 ppm PAC			60%
No. 5	RBS Feed	33		
	RBS Eff	64		
	RBS Eff + 10 ppm PAC			60%
No. 6	RBS Feed	33		
	RBS Eff	>69		
	RBS Eff + 20 ppm PAC			90%
	" " + 35 ppm PAC			90%
	" " + 50 ppm PAC			100%

*Survival in undiluted waste

TABLE II

ACTIVATED SLUDGE EFFLUENT TREATED WITH PAC

Parameter		Act Sludge Eff	Act Sludge Eff +100 ppm PAC
Toxicity (% Survival)		0 (24 hr)	100 (96 hr)
COD	mg/l	108	84
NH_3(N)	mg/l	35	28
Oil	mg/l	0.2	0.1
Naphthenic Acids	mg/l	1.5	0.6
Cr(T)	mg/l	0.02	0.02
Cu	mg/l	0.20	0.25
Zn	mg/l	0.03	0.02

TABLE III

ACTIVATED SLUDGE EFFLUENT TREATED WITH PAC

Carbon Dosage (ppm)	0	50	100	150
Parameter				
Toxicity (% Survival)	0	10	100	100
COD mg/l	150	130	120	120
Phenol mg/l	4.8	4.9	4.7	5.2
Oil mg/l	0.1	0.1	0.1	0.1
Naphthenic Acid mg/l	3.1	4.3	3.5	3.1

TABLE IV

EFFECT OF pH ON TOXICITY

RBS Effluent @ 7.2 pH	40% Survival
RBS Eff Lowered to 6.5 pH	0% Survival
RBS Eff Raised to 8.5 pH	90% Survival

TABLE V

EFFECT OF pH ON CARBON TREATMENT

RBS Feed 7.1 pH	36 TLm
RBS Feed @ 6.5 pH + 30 ppm PAC	65 TLm
RBS Feed @ 7.0 pH + 30 ppm PAC	61 TLm
RBS Feed @ 7.5 pH + 30 ppm PAC	80 TLm

TABLE VI

COMPARISON OF TWO CARBONS

Sample	Toxicity	TOC (mg/l)
RBS Effluent (as is)	58 TLm	68
RBS Eff + 60 ppm PAC-A	85 TLm	57
+ 90 ppm PAC-A	93 TLm	57
RBS Eff + 15 ppm PAC-B	93 TLm	57
+ 30 ppm PAC-B	90% Survival	54
+ 60 ppm PAC-B	100% Survival	44

TABLE VII

COMPARISON OF TWO CARBONS

PAC-A Added Continuously to RBS Pilot Plant and Additional PAC-A or PAC-B Added to RBS Effluent

RBS Eff + 45 ppm PAC-A	40 TLm
RBS Eff + 195 ppm PAC-A	86 TLm
RBS Eff + 45 ppm PAC-A + 50 ppm PAC-B	93 TLm
RBS Eff + 45 ppm PAC-A + 75 ppm PAC-B	100% Survival

TABLE VIII

GRANULAR CARBON TREATMENT OF TRICKLING FILTER EFFLUENT

	COD mg/l					Toxicity (Survival)				
			Column					Column		
Day	Feed	No.1	No.2	No.3	No.4	Feed	No.1	No.2	No.3	No.4
1	180	70	60	30	10		100	-	-	-
2	180	80	30	30	30		100			
3	180	100	50	30	40		90			
4	200	120	50	30	50		70			
5	260	210	140	80	90		0			
6	300	260	160	110	100					
7	-	240	170	100	70					
8	-	250	200	140	100					
9	270	270	220	170	140			100		
10	320	300	250	210	170	61TLm		100		
20	220	210	170	160	100	34TLm		0	100	
30	180	130	130	120	110	71TLm			100	
45		160	160	130	130	45TLm			80	
50		170	170	150	130				0	0
	Hot Water Wash									
55	190	160	120	120	120					100
60	150	140	140	130	100	53TLm			100	100
70	150	150	140	140	140	59TLm			0	100
75	Hot Water Wash									
100	170	170	160	130	130	45TLm			80	100

SESSION VIII

ADD-ON GRANULAR ACTIVATED CARBON

Chairman

Nicholas D. Sylvester

Professor of Chemical Engineering
University of Tulsa, Tulsa, Oklahoma

Speakers

Fred M. Pfeffer

W. Harrison and L. Raphaelian

"Pilot-Scale Effect on Specific Organics Reduction and Common Wastewater Parameters"

R. H. Zanitsch

R. T. Lynch

"Granular Carbon Reactivation-State of the Art"

L. W. Crame
"Activated Sludge Enhancement: A Viable Alternative to Tertiary Carbon Adsorption?"

"GRANULAR CARBON REACTIVATION: STATE-OF-THE-ART"

R. H. Zanitsch
Engineering Director, Calgon Environmental Systems Division

R. T. Lynch
Process Engineer, Calgon Corporation

Use of granular activated carbon for treatment of industrial wastewater is receiving widespread acceptance. In the past several years, 100 adsorption systems have been installed in industrial plants. Applications range from dye plant wastewater reuse to removal of toxic materials. Granular carbon is being used to treat flows as low as 1,000 gallons per day to as high as 20,000,000 gallons per day in industrial waste applications. It is being employed as a pretreatment step to remove toxic materials prior to biological treatment, as the main treatment process and for tertiary treatment of biological plant effluents.

In most industrial wastewater applications, cost of virgin carbon prohibits using it on a throw-away basis. Chemical regeneration is feasible in only a limited number of applications and regenerant disposal remains a problem. Thermal reactivation is in most cases complete, efficient, and economical whether it is performed on-site or on a contract basis at a central reactivation facility.

The technology of reactivation with industrial waste carbons has developed in only the last ten years. There are now approximately twenty reactivation systems installed in the United States which are reactivating industrial wastewater carbons.

New thermal reactivation processes (such as fluidized beds and electric furnaces) are now being developed but no commercial experience with industrial wastewater carbons has been developed in the United States. For the purposes of this presentation, we will discuss our experience with the design and operation of multiple hearth furnaces and rotary kilns as they relate to industrial wastewater applications.

THE THERMAL REACTIVATION PROCESS

Granular carbon is usually wet when fed to the reactivation furnace. Water concentration is a function of carbon size, water temperature during the dewatering step, and the amount of adsorbate on the carbon. In practice, moisture content varies from 40 to 50 percent on a wet spent basis.

The reactivation process can be divided into three steps:

1. Evaporation of moisture on the carbon (Drying).

2. Destructive distillation of organics resulting in pyrolysis of a portion of the carbon from the organic materials (Baking).

3. Activation of the carbon by selectively burning carbon deposited during the organic removal step (Activation).

During the drying step, carbon temperature is increased to approximately 212°F (100°C) and moisture evaporates into the gas phase. As moisture evaporates it is also possible for highly volatile organics to be steam distilled.

The second step is termed baking or pyrolysis of the adsorbate. During this step, carbon temperature increases to approximately 1200-1400°F (649-760°C). A portion of the organic molecules are thermally cracked to produce gaseous hydrocarbons which are driven off. The remaining lower molecular weight organics are distilled. During this process, a carbon char is deposited in the pore structure of the original activated carbon.

The final step is activation of the carbon - a chemical reactivation whereby carbon char deposited during the baking step is combusted along with a small amount of the original carbon. By this time, temperatures are in the range of 1600-1800°F (871-982°C).

Since the fixed carbon and the granules are both carbon, the process requires that fixed carbon be selectively gasified with minimum gasification of the granular carbon. Steam is added to the furnace and oxygen concentration is controlled to promote gasification of the fixed carbon while minimizing burning of the original granular carbon.

REACTIVATION SYSTEM DESCRIPTION

The basic sequence for thermal reactivation is as follows: (See Exhibit 1).

Spent carbon is removed from the adsorbers and transferred as a slurry to a spent carbon storage tank. Spent carbon is then transferred to an elevated furnace feed tank from which it is metered, at a controlled rate, to a dewatering screw. The dewatering screw is an inclined screw conveyor which serves the dual purpose of gravity draining slurry water from the granular carbon and providing a water seal for the top of the furnace. A timer operated valve is used to meter carbon to the dewatering screw. Drained, but wet, spent carbon then gravity flows into the furnace where it is dried, baked, and reactivated as discussed earlier. Reactivated carbon exits the furnace by gravity and enters a quench tank. The quench tank serves the dual purpose of wetting the reactivated carbon and providing a bottom seal for the furnace. The carbon is then transferred to a reactivated carbon storage tank from which it is then returned to the adsorbers as needed. In most industrial waste applications, an afterburner and scrubber are provided for destroying organics and removing residual particulates from the furnace off-gases.

The spent carbon storage tank should be designed for five to ten days storage of carbon in order to allow for routine furnace maintenance and unscheduled shut-downs. This is usually a lined carbon steel tank with a cone bottom to facilitate carbon flow. The reactivated carbon storage tank is usually sized in the same manner with the same materials of construction. In the case of the reactivated carbon storage tank, facilities should be provided for adding virgin makeup carbon to the system as required.

The furnace feed tank is usually sized for at least one shift of operation. The feed tank insures a constant carbon feed to the furnace independent of the large storage system. This tank is usually a cone-bottom, lined carbon steel tank.

Spent and reactivated carbon are transferred in slurry form using either eductors, blowcases or slurry pumps. In the case of eductors and pumps, dilution water must be provided in order to reduce slurry concentration to less than one pound per gallon to minimize carbon abrasion and line erosion. Eductors are generally applicable in non-corrosive services where static head is not great. Pumps can be used satisfactorily in high-head applications, but are subject to erosion and plugging. Eductors and pumps require use of dilution water which necessitates installation of water recycle systems. The blowcase is an efficient method of transferring carbon. Both air and water have been used to pressurize blowcases. In the case of a blowcase, carbon is transferred in a much denser slurry (three pounds per gallon) and, therefore, care must be taken to maintain control over line velocities to minimize abrasion and wear. Material for carbon slurry lines should be compatible with the wastewater. As long as slurry lines are flushed free of carbon after each transfer, galvanic corrosion of carbon steel lines will not be a problem; however, if the wastewater is corrosive, more exotic materials of construction should be used. All carbon slurry lines should be equipped with flush connections to facilitate flushing and unplugging.

CAPITAL AND OPERATING COST ESTIMATES

Based on our experience with the design, installation, and operation of multiple hearth furnaces and rotary kilns for reactivating industrial waste carbons, we have estimated the installed cost of reactivation systems to reactivate 5,000, 10,000, 30,000, and 60,000 pounds per day. (See Exhibit 2). The capital cost curve shown in Exhibit 3 represents a total installed cost including all equipment, site preparation, foundations, installation, startup, and indirects. We have assumed that necessary utilities and off-site facilities are available at the battery limits. As you can see, we estimate the total installed cost of a 10,000 pound per day reactivation system to be approximately $1.25 million plus or minus 20 percent. The time required to design, procure, install, and startup a reactivation system is usually estimated to be two years assuming a twelve-month delivery time on the furnace and associated equipment.

We have also estimated direct operating costs for reactivating 5,000, 10,000, 30,000, and 60,000 pounds per day of industrial wastewater carbons as shown in Exhibit 4.

In order to develop these costs, the following elements were considered:

1. Labor was estimated to be one operator per shift at a rate of $10/hour. An allowance of 25 percent of the labor cost for supervision was also included.

2. Fuel was estimated at 8,000 BTU's per pound at a cost of $3/million BTU's. This estimate includes afterburner operation and an allowance for inefficiencies due to interruptions and reduced feed rates. Approximately half of the fuel consumption is required for the afterburner and idling.

3. Power costs for the reactivation system are minimal and were assumed to cost $0.03/KWH.

4. Steam costs were based on an average demand of one pound of steam per pound of carbon for reactivation at a cost of $4/1,000 pounds.

5. Maintenance costs for an industrial wastewater application can range from 8 to 15 percent of the reactivation system cost per year. For this estimate, we assumed a maintenance cost of 8 percent per year.

6. Makeup carbon costs were based on an average carbon loss rate of 7 percent and a virgin carbon cost of $0.57/pound delivered. Carbon losses can range from as low as 3 percent to greater than 10 percent depending on design and operation of the system. Most industrial waste systems operate in the 5 to 7 percent loss range. Makeup carbon costs represent the highest individual cost element in the direct operating cost estimate and, therefore, all efforts should be made to minimize carbon losses through good design and operation.

7. A general plant overhead of 10 percent of the above cost was allowed to cover such items as insurance, taxes, monitoring, accounting, and administration.

As can be seen from Exhibit 4, the direct operating cost for a reactivation system handling industrial wastewater carbons ranges from $0.11 to $0.19/pound over the range investigated. This does not include depreciation or amortization of investment. The economies of scale are obvious. We feel these costs can range plus or minus 20 percent, but in general, reflect the cost to operate a reactivation system on industrial waste applications.

MULTIPLE HEARTH FURNACE

Exhibit 5 is a cross-sectional view of a multiple hearth furnace. The furnace consists of a cylindrical refractory-lined steel shell containing several refractory hearths and a central rotating shaft to which rabble arms are attached. From four to eight hearths are used in carbon reactivation furnaces. The center shaft and rabble arms are cooled by air supplied by a centrifugal blower discharging air through a housing into the bottom of the shaft. A sand seal at the top of the furnace and a sand or water seal at the bottom are used to seal the furnace against introduction of extraneous air.

In operation, wet spent carbon is introduced through a chute into the outside of the top hearth of the furnace. The rabble arms are equipped with solid alloy rabble teeth which rake the carbon towards the center where it drops to the hearth below. The teeth on the rabble arms are arranged to move the carbon in a spiral path. The action is gentle to minimize attrition. The top hearth is termed an "in" hearth since carbon flow is inward.

The second hearth is consequently an "out" hearth where the carbon is moved outward by the rabble teeth. Out hearths have a series of holes around the periphery of the hearth through which the carbon drops to the next lower hearth.

In this manner, carbon passes through the furnace until it is finally discharged through a chute in the bottom hearth into the water filled quench tank. The chute extends under the water level in the quench tank to provide a seal.

Drying is accomplished in the upper one-third of the furnace. Distillation and pyrolysis of the adsorbate occurs in the next one-third. Activation of the carbon is completed in the bottom one-third of the furnace.

Burners are mounted tangentially on the furnace shell in burner boxes. Usually burners are placed on the bottom two or three hearths and on one upper hearth below the lowest drying hearth. However, if desired, burners can be mounted on any hearth including the drying hearths.

On small furnaces, two burners per fired hearth are used. On larger furnaces, three burners are installed. The burners are of the nozzle-mix type burning fuel oil or natural gas. Dual fuel burners are commonly employed to burn gas when it is available and fuel oil at other times.

Steam addition ports are provided on the bottom two or three hearths to add steam for control of the reactivation process.

The center shaft is driven through a variable speed drive at 0.5 to 2.5 rpm.

A number of furnaces have been installed with integral or "0" hearth afterburners. This is less costly from a capital cost standpoint than the separate afterburner.

DIRECT FIRED ROTARY KILN

Exhibit 6 is a simplified sketch showing a direct-fired rotary kiln. The kiln is a refractory lined steel shell enclosed on each end with refractory lined stationary hoods. This sketch depicts a counter-current operation where gas flow is opposite the carbon flow. Co-current operation is also possible and one carbon reactivation kiln is currently operating in this manner.

The kiln is mounted on two or three sets of trunions depending on the length of the unit. The kiln is sloped from the feed to the discharge end and one set of thrust rolls are used to maintain the kiln in position on the trunions. Proper training and alignment of trunions is important to minimize excessive wear of the trunions and tires.

The kiln is driven through a variable speed drive coupled to a speed reducer and pinion gear which meshes with a bull or girt gear mounted on the kiln shell. The kiln is equipped at each end with hoods. Rotary seals are used to seal between the rotating kiln shell and the stationary hoods. The hoods are refractory lined.

A feed screw or chute is used to feed wet carbon into the kiln. Flights are usually employed to advance the damp carbon and to shower the carbon in the feed end to obtain high heat transfer rates during the evaporation step. Flights are also used in the first portion of the baking step up to a point where the temperature reaches approximately 1200-1400°F (649-760°C). Material of construction for the flights is a function of carbon corrosiveness and reactivation conditions in the kiln.

The hot reactivated carbon, at a temperature of 1600-1800°F (871-982°C), discharges from the kiln and falls down the discharge chute into a water-filled quench tank. The discharge chute extends under the water level in the quench tank to form a seal to eliminate air leakage into the kiln.

A burner is mounted in the discharge hood to provide heat for the reactivation process. Either fuel oil or gas may be burned. The burner air-to-gas ratio is adjusted to minimize oxygen concentration in the kiln. A steam addition port also is provided in the discharge hood to admit steam into the kiln for control of the reactivation process.

The exhaust gases, at a temperature of 500-800°F (260-427°C), leave the kiln through a duct connected to the feed hood. In most installations, gases are passed through an afterburner for complete combustion of organics and burning of carbon fines swept out of the kiln. New installations, as is the case with the multiple hearth furnace, will probably require installation of a wet scrubber to meet air pollution codes in most areas of the country.

In a rotary kiln, reactivation process is controlled by varying the kiln speed to provide adequate retention time and by adjusting the steam rate and burner temperature at the settings required for the particular carbon to be reactivated. A steam rate of 0.6-1.2 pounds per pound of carbon and a temperature of 1600-2000°F (871-1093°C) are ranges encountered in practice.

OPERATING AND MAINTENANCE PROBLEMS

A number of unique operating and maintenance problems have been experienced in reactivating industrial wastewater carbons. These problems include:

Corrosion
Slagging
Poor Reactivated Carbon Quality
High Carbon Losses
Feed Interruptions
Hearth Failures
Slurry Line Erosion and Corrosion

Corrosion

Selection of proper construction materials for carbon storage and handling systems is very important. We have found lined carbon steel tanks to be satisfactory, but proper selection and application of lining material is extremely important. Lining material should be corrosion and abrasion resistant. We recommend thorough corrosion coupon testing prior to making a final selection. Erosion of lining material at carbon outlet nozzles, followed by corrosion of the metal, has been a problem. We have installed sacrificial wear plates or stainless steel cones on tanks in order to minimize this problem. Dewatering screws and quench tanks are generally constructed of 304 or 316L stainless steel. In general, these materials are satisfactory for most applications. However, the dewatering screw is exposed to the spent carbon slurry and, therefore, its material must be compatible with the wastewater. Corrosion of rabble arms and teeth in multiple hearth furnaces and lifting and drying flights in rotary kilns can be a problem when handling chlorinated hydrocarbons and organic sulfur compounds. Special attention must be given to material selection to minimize this problem.

Slagging

Formation of clinkers and slag in the furnace is generally a function of sodium and/or organic phosphate content of the spent carbon. Slag formation can be minimized by pretreatment of carbon and maintenance of proper furnace conditions. Formation of slag can generally be attributed to constituents in the water contained in the pores of the carbon as it enters the furnace. These chemicals react with alumina and silica in the furnace refractory resulting in slag formation.

Hearth Failures

Hearth failures in multiple hearth furnaces can generally be attributed to cyclic operation. Frequent feed interruptions, resulting in temperature excursions on the upper hearths, will weaken hearths and ultimately lead to failure. By minimizing the number of feed interruptions and maintaining continuous furnace operation, upper hearth life can be maintained for three to five years. Another problem leading to hearth failure is brick attack by sodium compounds; which leads to the slagging problem discussed earlier. Also, improper dewatering or improper operation of the dewatering screw, which would result in excessive amounts of water entering the top hearth, can result in thermal shock which leads to failure. In general, hearth life is a function of the operating philosophy of the furnace. If frequent feed interruptions due to improper carbon feed system design or cyclic operation are encountered, poor hearth life can be expected.

Carbon Losses

As mentioned earlier, makeup carbon cost is the single most important cost element for a reactivation facility. By properly designing the adsorbers, the carbon transfer and handling systems and the carbon storage and reactivation systems, losses can be controlled at the 5-7 percent level. Within the reactivation furnace itself, carbon losses should not exceed 1-3 percent. Carbon which is lost is due to oxidation during the activation step. This can be controlled by maintaining oxygen levels in the activation zone at 0-2 percent, or roughly that required for destruction of organics without sacrificing carbon. Most carbon losses in a granular carbon system occur due to backwashing of carbon in adsorbers, abrasion in slurry lines, spillage, and carryover in overflow lines. These losses can all be minimized by proper design of the basic system. Care must be given to overflow rates, backwash rates, and slurry line velocities, and frequent checks must be made to see that good housekeeping and operating techniques are being followed.

Slurry Line Erosion and Corrosion

As mentioned earlier, construction material of spent carbon slurry lines should be compatible with the wastewater in order to minimize corrosion. If spent carbon or reactivated carbon is allowed to accumulate in a carbon steel slurry line, galvanic corrosion can be expected. Therefore, flushing of all slurry lines after each transfer is recommended. If the wastewater is extremely corrosive, we recommend lined steel or stainless steel slurry piping be considered.

Erosion of slurry lines can be attributed to excessive transfer velocities. We recommend a slurry line velocity of 3-5 feet per second which is sufficient to prevent settling and minimize abrasion. Also, slurry lines should be as direct as possible with a minimum number of bends. We recommend that long-radius bends be used to minimize abrasion. Also, we recommend that all bends be accessible for periodic inspection and replacement. Flush connections should be provided at frequent intervals on all slurry lines in case a line becomes plugged.

FURNACE SELECTION CRITERIA

Choice of a reactivation furnace depends on many factors. A thorough analysis of each type of equipment plus reactivation characteristics of the carbon are necessary to make a final decision on which piece of equipment to use.

Both multiple hearth furnaces and kilns are being employed to reactivate granular activated carbon used in industrial wastewater treatment. The quality of reactivated carbon that can be achieved is the same for both units.

Major parameters influencing the selection of a reactivation furnace are as follows:

1. Capital Cost - Total installed costs for either a multiple hearth furnace or a rotary kiln are approximately the same. The purchase price is generally higher for a multiple hearth furnace. However, the installation costs are lower which tends to make installed costs the same. Site preparation, foundations, and structural costs are higher for a rotary kiln because of the greater area required to install a kiln.

2. Area Requirements - Area requirements are much greater for a rotary kiln than for a multiple hearth furnace. The kiln also requires more foundations and structural steel for walkways than a multiple hearth furnace. The multiple hearth furnace is higher than a kiln which means more structural steel is required to support the carbon feed equipment.

3. Fuel Consumption - Fuel consumption is higher in a rotary kiln because of higher heat losses. In a multiple hearth furnace, insulation is used behind the wall brick to minimize heat loss. This is not possible in a rotary kiln. Surface area is also higher in a rotary kiln than a multiple hearth furnace of equivalent capacity. Fuel consumption for each will be in the following ranges depending on capacity and operating rate as a fraction of rated capacity.

	BTU/LB Carbon*
Multiple Hearth Furnace	2500-4500
Rotary Kiln	3500-8000

*Does not include afterburner fuel requirements.

4. Capacity Turndown - Capacity turndown ratio is defined as the percent of rated capacity at which the furnace can be operated while producing good reactivated carbon with reasonable carbon loss. Capacity turndown for the equipment being evaluated in this paper are as follows:

   Multiple Hearth Furnace - 33 Percent
   Rotary Kiln - 50 Percent

   The multiple hearth furnace can be operated at a lower fractional capacity because of the greater degree of control that can be obtained in various zones of the furnace. In a rotary kiln, with only one burner and one steam addition point, kiln speed is the major parameter that can be varied to operate at lower capacities.

5. Degree of Control - Better reactivation process control can be achieved in a multiple hearth furnace because the furnace is divided into distinct zones according to the number of hearths in the furnace. Each hearth can be equipped with burners, steam addition, and air addition which can be controlled independently. Thus, it is possible to control temperature and vary the atmosphere in each hearth to optimize carbon reactivation.

   In a rotary kiln, the steam port, and burner can only be mounted in the firing end of the kiln. With this arrangement, the degree of control that can be achieved is less than in a multiple hearth furnace. In a properly sized kiln, this is not a distinct disadvantage and good carbon reactivation can be achieved. However, as discussed previously, capacity turndown is not as great in a kiln.

6. Corrosion and Slag - Many industrial waste streams contain inorganic impurities which can cause corrosion and slag formation in the reactivation furnace. These impurities are mostly chloride and sulfur salts of calcium and sodium. The multiple hearth furnace has more exposed alloy parts than a kiln and is, therefore, more susceptible to corrosion. Rabble teeth and arms are expensive, long delivery castings as opposed to the alloy flights in a kiln which are fabricated from readily available plates. Also, considerable corrosion of flights can occur in a kiln before replacement is required.

   Slag buildup in a multiple hearth furnace will require periodic shutdowns to remove accumulated material. Slag in a rotary kiln will be discharged, with the reactivated carbon, into the quench tank where it can be removed without shutting down the process.

7. Maintenance - Experience with reactivating industrial wastewater carbons indicates higher maintenance costs in a multiple hearth furnace. The factors responsible are:

   a. Corrosion and slag formation resulting in shutdowns for repairs.

   b. Rabble teeth and arms are more expensive to replace than alloy flights used in a rotary kiln.

   c. Multiple hearth furnaces are more difficult to work on. It takes more man-hours to rebuild a hearth than to replace brick in a kiln. Because of these factors, downtime to affect repairs is longer in the multiple hearth furnace.

   d. More instrument components are required with a multiple hearth furnace.

8. Effect of Feed Outages - The upper hearths in a multiple hearth furnace can be damaged from temperature cycling caused by interruptions in furnace feed. Periodic planned shutdowns can be conducted without hearth damage.

   Feed outages are usually not a major problem in a rotary kiln. The refractory is much less effected by temperature cycling in a kiln than the hearth refractory in a multiple hearth furnace.

9. Operating Factors - Operating factors for kilns and multiple hearth furnaces are as follows:

Rotary Kiln	85-95 Percent
Multiple Hearth Furnace	75-90 Percent

Multiple hearth furnaces must be shutdown more often to clean slag and replace rabble teeth. When a furnace is down for repairs, the work requires more man-hours to complete than similar work on a rotary kiln.

Based on the above parameters, the multiple hearth furnace offers the following advantages over a rotary kiln:

- Better control of temperature and atmosphere
- Lower fuel consumption
- Greater capacity turndown

- Less area required
- Lower carbon losses from carryover and attrition

The rotary kiln advantages are:

- Less corrosion and slag formation
- Less downtime
- Lower maintenance costs and easier maintenance
- Less effect from feed outages
- Easier to operate

SUMMARY AND CONCLUSIONS

Granular activated carbon has been demonstrated to be effective in treatment of a wide variety of industrial wastewaters. Both multiple hearth furnace and rotary kilns can satisfactorily reactivate spent carbons used in industrial wastewaters provided adequate consideration is given to selection of materials, sizing of equipment, and operating philosophy. Experience gained over the last ten years indicates that corrosion, slagging, poor reactivation quality, carbon losses and line erosion can all be minimized through good design. Although the same types of problems exist in industrial purification and municipal water and waste treatment applications using granular activated carbon, they are magnified in industrial wastewater applications where wastewater quality, and thus carbon exhaustion rates, are more variable and substantially more corrosive. However, our experience with reactivating over 100,000,000 pounds of spent carbon for more than 75 different industrial wastewater applications, indicates that a high quality product can be produced on a reliable, economical basis.

BIOGRAPHIES

Roger H. Zanitsch is Engineering Director of the Calgon Environmental Systems Division for Calgon Corporation. He joined Calgon as a Project Engineer in 1969 and was later named Project Manager of the Environmental Engineering Department. Zanitsch received his BS degree in Civil Engineering from the University of Cincinnati and an MS degree in Environmental Engineering from the same school. Zanitsch is a member of the Water Pollution Control Federation.

Richard T. Lynch is a senior engineer in the Process Engineering Group of Calgon Corporation's Engineering Department. He has a B.S. degree in Chemical Engineering from the University of Florida. He has been a project manager for the design of several carbon adsorption reaction systems treating industrial waste streams. He is a member of the American Institute of Chemical Engineers and a registered professional engineer in Florida.

EXHIBIT 1

TYPICAL REACTIVATION SYSTEM FLOW DIAGRAM

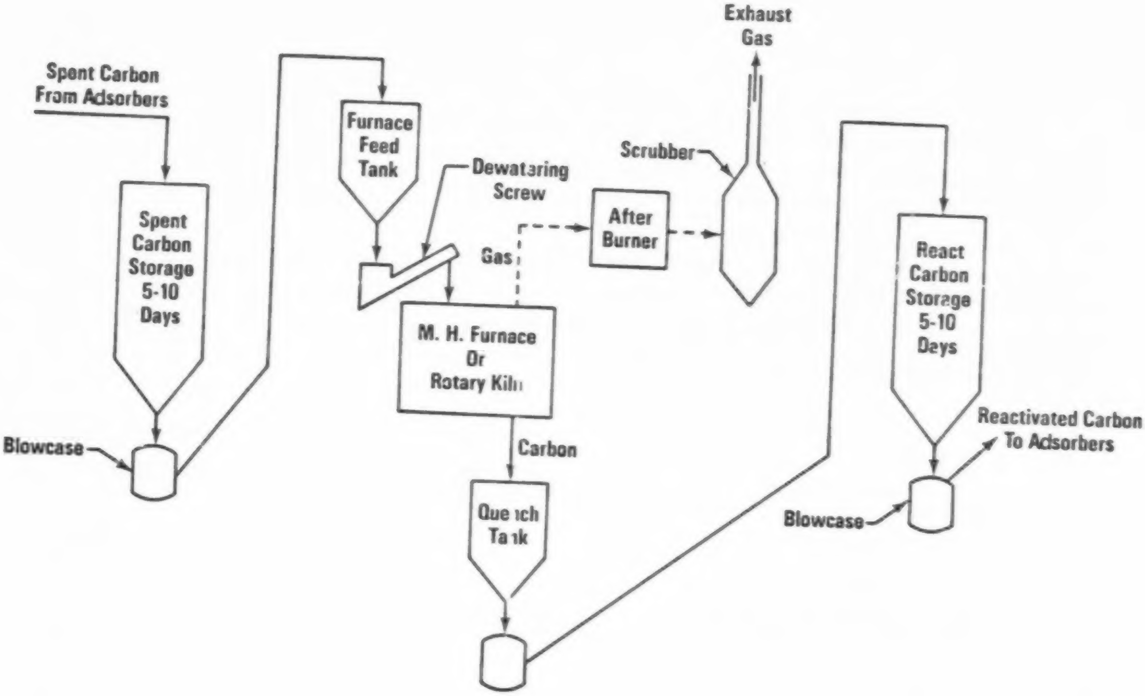

Spent Carbon From Adsorbers
Spent Carbon Storage 5-10 Days
Blowcase
Furnace Feed Tank
Dewatering Screw
Gas
M. H. Furnace Or Rotary Kiln
Carbon
Quench Tank
After Burner
Scrubber
Exhaust Gas
React Carbon Storage 5-10 Days
Reactivated Carbon To Adsorbers
Blowcase

EXHIBIT 2

INSTALLED COSTS OF REACTIVATION SYSTEMS

CAPITAL COSTS

	Reactivation Rate - 1,000 Lbs/Day			
	5,000	10,000	30,000	60,000
Capital Cost Estimate ($ Million)				
Purchased Equipment	0.24	0.36	0.77	1.20
Installation*	0.61	0.91	1.93	3.00
	0.85	1.27	2.70	4.20

*Installation costs include foundations, structural equipment setting, electrical, instrumentation, site preparation, engineering contractor, overhead and profit, and indirects.

OPERATING COSTS

	Reactivation Rate - 1,000 Lbs/Day			
	5,000	10,000	30,000	60,000
Fuel - 8,000 BTU/Lb @ $\$3/10^6$ BTU	45	90	265	525
Power @ 3¢/KWH	10	20	50	80
Steam - 1.0 Lb/Lb @ $4/1,000 Lbs	10	15	45	90
Labor @ Supervision	110	110	110	110
Makeup Carbon - 7% @ 57¢/Lb	70	145	435	875
Maintenance @ 8% Capital	70	100	215	335
General Plant Overhead	30	50	110	200
Total Operating Cost ($1,000/Yr.)	345	530	1,230	2,215
Operating Cost ¢/Lb Carbon	18.8	14.5	12.2	11.0

EXHIBIT - 3

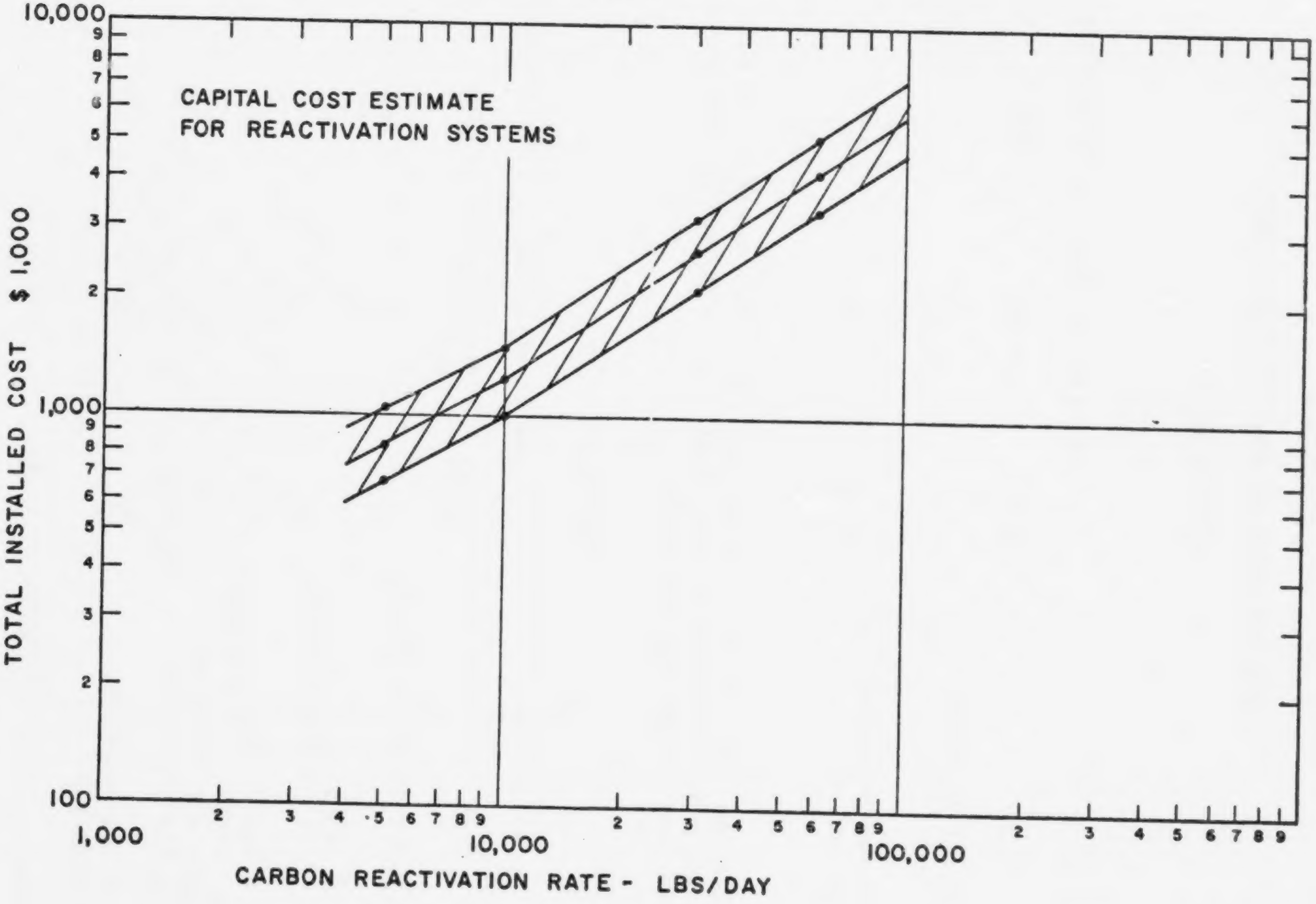
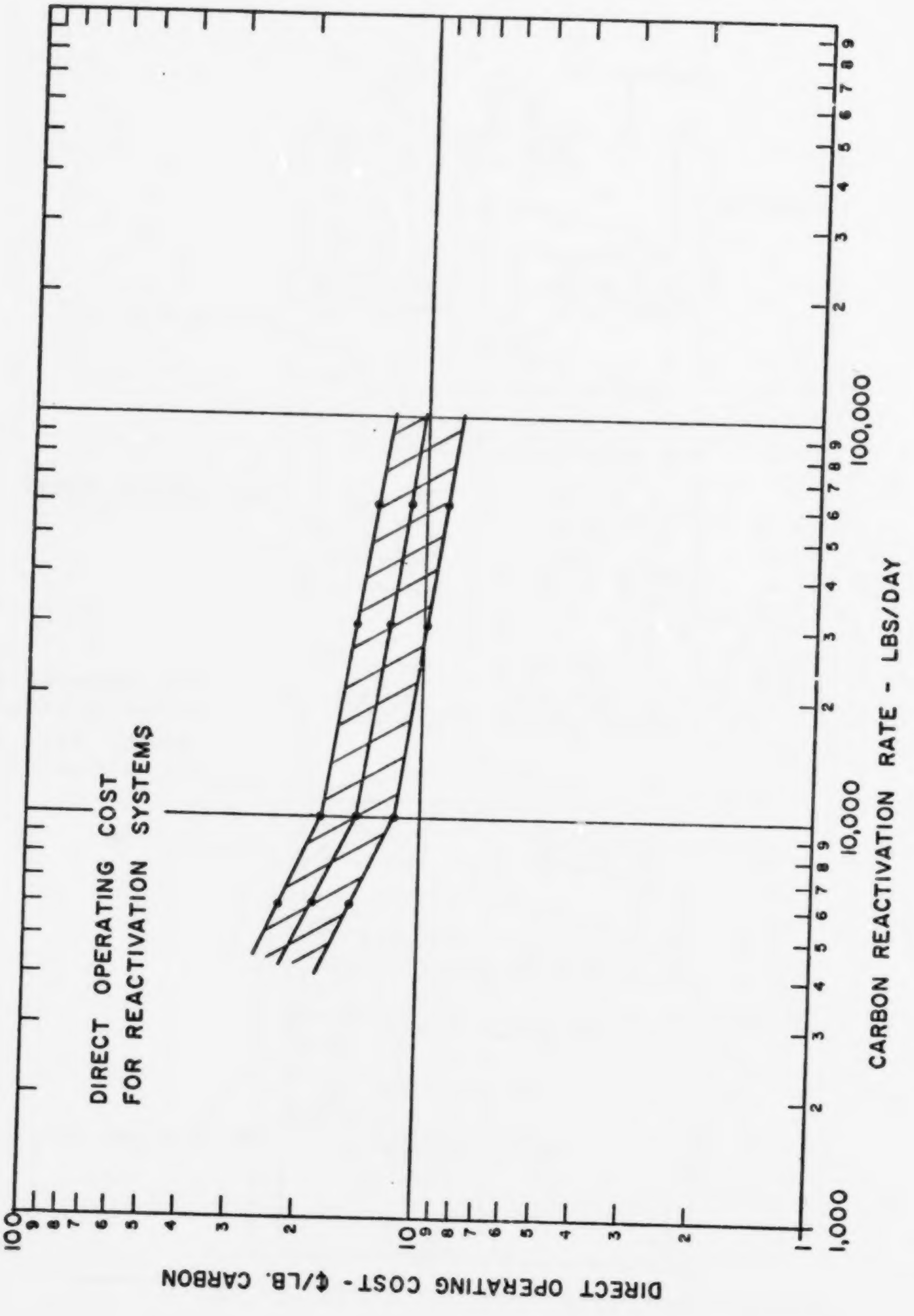
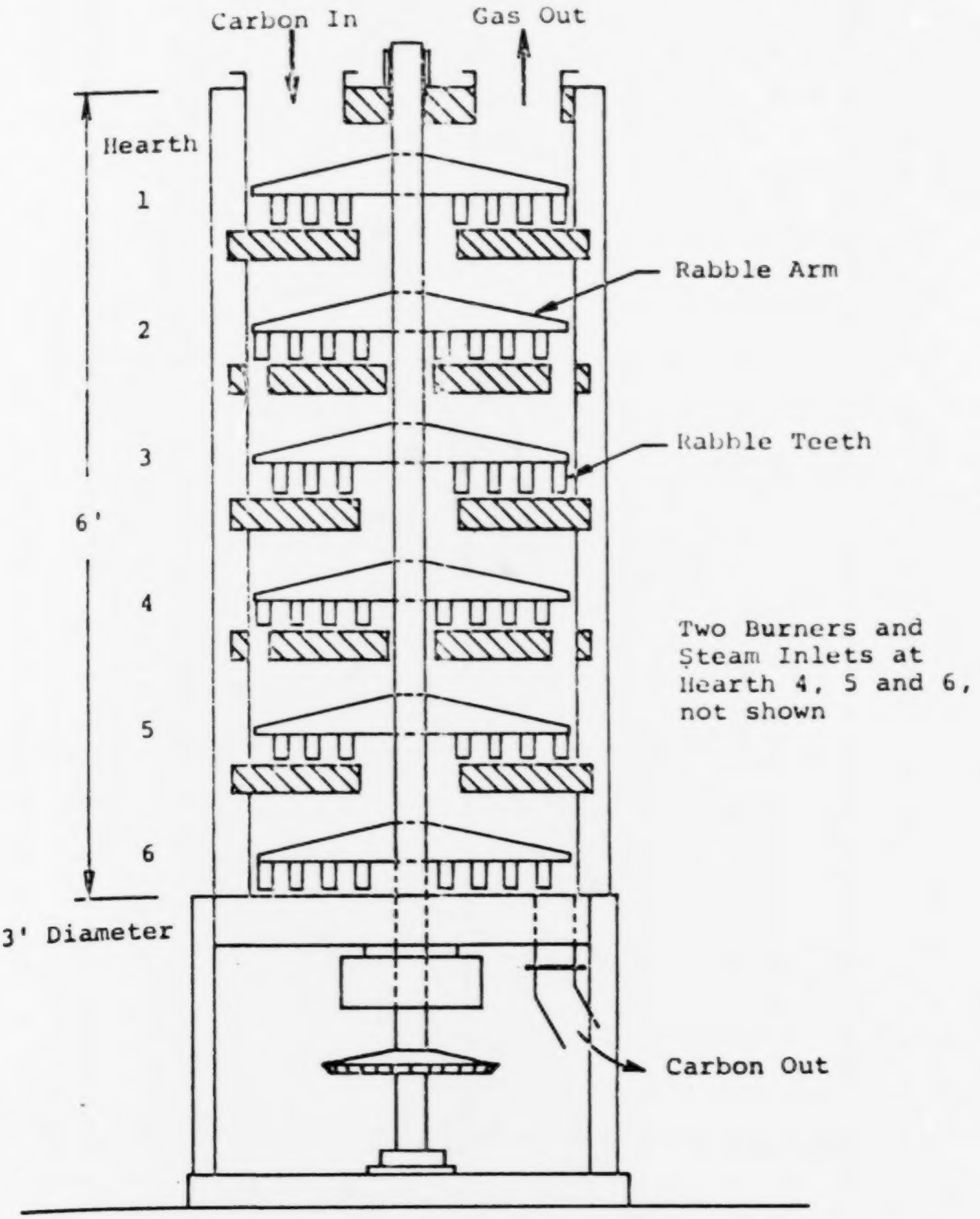

CAPITAL COST ESTIMATE
FOR REACTIVATION SYSTEMS
TOTAL INSTALLED COST $ 1,000
10,000
1,000
100
9
8
7
6
5
4
3
2
CARBON REACTIVATION RATE - LBS/DAY
1,000
10,000
100,000
2
3
4
5
6
7
8
9

EXHIBIT - 4



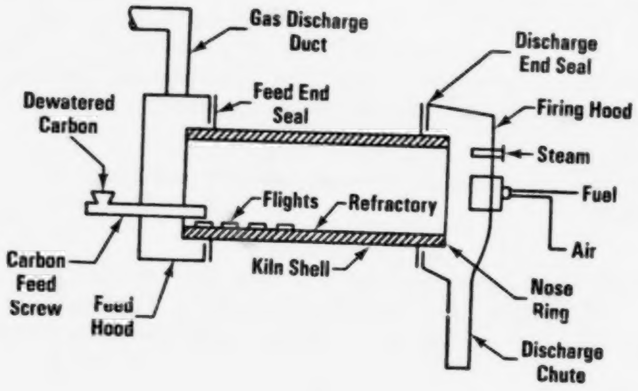
DIRECT OPERATING COST
FOR REACTIVATION SYSTEMS

EXHIBIT 5


Carbon In
Gas Out
Hearth
1
2
3
4
5
6
6'
3' Diameter
Rabble Arm
Rabble Teeth
Two Burners and Steam Inlets at Hearth 4, 5 and 6, not shown
Carbon Out

CROSS SECTIONAL VIEW OF MULTIPLE HEARTH FURNACE USED AT POMONA WATER RECLAMATION PLANT

EXHIBIT 6


Gas Discharge Duct
Discharge End Seal
Feed End Seal
Dewatered Carbon
Firing Hood
Steam
Fuel
Flights
Refractory
Air
Carbon Feed Screw
Kiln Shell
Nose Ring
Feed Hood
Discharge Chute

DISCUSSION

L. L. Krohn, Union Oil Co.: Have you made an analysis of the off-gases from that furnace?

Roger Zanitsch: Yes, we have. We've looked at in excess of 100 different industrial waste carbons. We've analyzed the off-gases before and after afterburning on many of these, to determine what temperature and residence time is needed for organic destruction.

L. L. Krohn, Union Oil Co.: Do you have any feel for the particulate matter coming out?

Roger Zanitsch: We have systems operating that are designed with a 2 second residence time which is primarily there to consume the particulates. If you have a half second residence time which is certainly sufficient to destroy most of the organics present, you'll still have some carbon fines that will need to be scrubbed. We feel that the 1-2 second residence time at 1800°F can destroy the carbon fines as well as the organics.

L. L. Krohn, Union Oil Co.: Considering the new source review - can we hope to build this system?

Roger Zanitsch: Reactivation furnaces are now in operation and many are being designed for industrial waste applications. Technology exists to handle essentially all air pollution control requirements at a reasonable cost.

Mac McGinnis, Shirco, Inc.: We have made some of the economics that you're talking about for our electric regeneration furnace and compared them with similar economics as you have presented here from multiple hearth and other approaches and just a couple of comments - a couple of factors that we have included that you haven't mentioned are in the area of utilities, scrubber water which on small capacity units may be a fairly significant contribution of operating costs; and the other factor you mentioned quality of the product, laboratory labor, lab time to confirm that the product is indeed of the desired quality, can be a fairly significant contribution.

Roger Zanitsch: I'm glad you brought this up. In the analysis that I showed, the operating cost included a 10% general plant service allowance on the total operating cost to cover overhead items such as accounting, quality control, etc. As far as scrubber water cost and disposal, it can be a factor. In those installations where we have scrubbers, we've recycled water through the pretreatment system to remove the carbon fines. Frankly, we haven't found this to be a significant cost factor.

DISCUSSION

Mac McGinnis, Shirco, Inc.: Well, a half cent here and half cent there, it begins to add up. The other general comment is you've indicated that there is considerable data on regeneration costs in multiple hearth furnaces in particular and you've showed us some trend lines in terms of direct operating costs. Can you comment on any specific data, you know, accumulated over a period of time that indicates an actual cost figure for some specific application?

Roger Zanitsch: The numbers which I presented are based on our experience in operating both small and large furnaces.

Mac McGinnis, Shirco, Inc.: One last comment - would you say then that the actual data would fall within that plus or minus 20% about your nominal curve?

Roger Zanitsch: On industrial waste applications, yes. In process applications, such as the decolorization of sugar solutions, operating costs are substantially lower since they have a constant feed and a very predictable product.

Colin Grieves, Amoco Oil Co.: First, would you care to comment on some of the new technology which you eluded to? And second, would you like to say anything about regeneration of powdered activated carbon?

Roger Zanitsch: As far as the new technologies are concerned, I was personally thinking of the electric furnace and the fluidized bed furnaces. The Japanese have several different types of furnaces. Most of the experience with the newer furnaces has been in either pilot-scale or on the commercial scale, but in considerably less corrosive application than you have in industrial wastes. In industrial waste applications, the big awakening has been in the areas of corrosion, maintenance costs, and feed interruptions. The new technologies have not been demonstrated in this type of service. As the new technology develops, it's going to take some time to gain the experience necessary to apply these new furnaces in the industrial waste effort. As far as powdered carbon activation, I don't really feel qualified to discuss it on the basis that I would only be expressing my opinions since no commercial experience has been developed.

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